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Bacterial Production and Contaminant Mineralization in Sediments of the Ala Wai Canal, Oahu, Hawaii

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14. ABSTRACT

The Ala Wai canal is a small, man-made estuary that was dredged from August 2002 to October 2003 to increase water circulation and oxygen deficit in bottom waters. Rates of bacterial growth (heterotrophic production) and carbon metabolism (^{14}C-substrate mineralization) were measured on surface sediments and core sections during three sampling events before, during, and after dredging. Heterotrophic production increased at all stations during the post-dredge sampling relative to the pre-dredge sampling. Lignin analysis indicated most of this organic matter was terrestrially derived (woody and non-woody angiosperms). Carbon substrate mineralization rates were typically highest between the confluence with the Manoa-Palalo outfall and the canal mouth, with overall rates decreasing for catechol >> 2,4,6-trinitrotoluene > phenanthrene > naphthalene > fluoranthene. Polycyclic aromatic hydrocarbon (PAH) mineralization was relatively low compared with other urbanized watersheds. Even with enhanced flow associated with the dredging operation, it is probably unlikely that significant amounts of PAHs are being exported from the canal to the adjacent coastal waters.

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Introduction:

The Ala Wai canal is a man-made, tropical estuary on Oahu, Hawaii that was originally constructed from 1921-1928 to drain the local swamp and create land suitable for the commercialization of Waikiki (see historical review by Glenn and McMurtry 1995). The primary sources of freshwater to the Ala Wai canal are the Manoa-Palalo Drainage Canal (draining the Manoa and Palalo Valleys), Makiki Stream (draining the Makiki Valley) and a storm water drain at the end of the canal. Pacific Ocean water tidally intrudes as a salt wedge that extends the entire canal length and into the Manoa-Palalo Drainage Canal (Glenn and McMurtry 1995). Brackish water from an approximately one-meter thick surface layer flows seaward out of the canal creating a compensating flow via the marine bottom waters (Gonzalez 1971, Glenn and McMurtry 1995). From a channel ca. one kilometer long, the canal empties into the Ala Wai Small Boat Harbor and then the Mamala Bay (Glenn and McMurtry 1995). Inland from this seaward channel is a small basin, a silt sill formed from settling particles from the Manoa-Palalo Drainage Canal, and a second basin at the terminus of the canal (Glenn and McMurtry 1995) (Figure 1). The silt sill was dredged in 1966, 1978, and 2002, to enhance water circulation and reduce anoxia (0 % dissolved oxygen saturation) in the bottom waters and surface sediments (Glenn and McMurtry 1995).

The canal's anoxia and reduced circulation results from low freshwater input to the waterway relative to tidal input (Laws et al. 1993). The Ala Wai behaves like a type B estuary as the tidal prism volume (V_p) is 10 to 20 times the volume of freshwater input (V_f) (Biggs and Cronin 1981) (specifically, Ala Wai $V_p/V_f = 16$; Gonzalez 1971, Laws et al. 1993). This class of estuary is typically has little sediment export to ocean (Biggs and Cronin 1981). Sedimentation rates of 7 to 8 x 10^3 m^{-3} yr^{-1} were calculated from the amount of material removed during the 1966 and 1978 dredging events (Gonzalez 1971, Laws et al. 1993). Using ^{137}Cs-based methods, McMurtry and coworkers (1995) calculated fill times of 40-70 years depending on the location through the canal. The primary source of this sediment is surface runoff related to flash floods from short, intense rain events common to this watershed (Tomlinson and De Carlo 2003). Included in this runoff are nutrients that stimulate phytoplankton growth, as well as, metals (Luoma 1974, Spencer et al. 1995, Sutherland 1999a, De Carlo and Anthony 2002, De Carlo et al. 2004), minerals (Fan et al. 1995) and organic contaminants associated with urban surface runoff (Fujiwara 1973 as cited in Freeman and Fox 1995, DeCarlo and Spencer 1995, 1997, Pellenbarg et al. 1997).

Nutrients supplied to the canal during the rain events include phosphate, nitrate, silica, and ammonium (Miller 1975, Laws et al. 1994) which can normally be limiting nutrients for primary production in aquatic ecosystems. Nutrient inputs typically enter canal surface waters via the Manoa-Palalo Drainage Canal, Makiki Stream, and large storm drain at the end of the canal (Miller 1975, Laws et al. 1994). These nutrients have been estimated to support high gross photosynthetic rates (3.9-5.5 g C m^2 d^{-1}) that increase three- to four-fold from the mouth (Harris 1975, Laws et al. 1993). The dominant phytoplankton taxon is the diatom, *Skeletonema costatum* Greville (Cleve), with its highest abundance in the basin between the underwater sill at the Manoa-Palalo confluence and canal terminus (Beach et al. 1995). Given the high nutrient inputs from runoff and the high turbidity in the canal, photosynthetic rates appear to be light rather than nutrient limited (Laws et al. 1993).

Water column stratification and limited water circulation combine with high primary production to lead to large diel variations in dissolved oxygen concentration. Surface water typically is supersaturated with dissolved oxygen (DO) during the day and hypoxic (<20% DO saturation) at night (Laws et al. 1993).

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Uptake of CO_2 from the water column by phytoplankton and the resulting increase in water pH during high primary production events is postulated to precipitate inorganic carbon from the water column to the surface sediments via biogenic-induction (Glenn et al. 1995). Particulate organic matter (POM) derived from phytoplankton biomass eventually settles, supporting high biological DO demand in the bottom waters and surface sediments. Autochthonous POM input to the sediment is exceeded by allochthonous input by about 60 %. Approximately 18 % of the total POM settles in the surface sediment, 12 % is exported from canal to Mamala Bay while respiration consumes about 70 % (Laws et al. 1993). Elevated heterotrophic respiration in bottom waters and sediment results in periodic anoxia (Laws et al. 1993) which can reduce biological mixing by benthic macrofauna (De Carlo and Anthony 2002) and diversity of benthic meiofauna (Resig et al. 1995).

Though nutrients and much of the POM are utilized by primary and secondary producers in the Ala Wai canal, respectively (Laws et al. 1998), some pathogenic bacteria (Rose et al. 1997) and viral particles (Culley and Steward 2007) are exported offshore to Mamala Bay (Connolly et al. 1999) and into deep waters (Laws et al. 1999). POM that is neither respired nor exported (*ca*. 3100 tons annually; McMurtry et al. 1995) makes up much of the canal's surface sediment (typically 5-7 % OM w/w, Glenn et al. 1995) where it alters bathymetry and further reduces water circulation. Sediment accumulation has led to the decision by the local municipality to dredge portions of the Ala Wai canal three times since its construction. Dredging was intended to remove pollutants and POM associated with existing accumulated sediments and increase water circulation and oxygenation in the bottom waters and post-dredge surficial sediments (Gonzalez 1971, Department of Land and Natural Resources, State of Hawai'i 1990, Lum and Cox 1991, Laws et al. 1993, Glenn et al. 1995). Some recent studies focusing primarily on chemistry and toxicity suggest that dredging can accomplish these goals with minimal negative impact on the biological community (Guerra et al. 2009).

Most dredging effects studies on marine and estuarine ecosystems involve aquatic plants and seagrasses (Brookes 1987, Erftemeijer and Lewis 2006) or benthic macrofauna (Newell et al. 1998, Piersma et al. 2001, Newell et al. 2004, Sa´nchez-Moyano et al. 2004, Boyd, S.M. et al. 2005, Robinson et al. 2005, Smith et al. 2006, Szymelfenig et al. 2006, Cooper et al., 2007). Fewer examine the effect of removal actions on microalgae (Lewis et al. 2001, Licursi and Gomez 2009) or heterotrophic bacteria (Bozena and Dudkowiak 2007). Studies of periphyton have reported changes in community composition with increases in abundance of pollution-tolerant bacteria (Licursi and Gomez 2009) and microalgae but decreases in their species diversity (Lewis et al. 2001). By examining changes in bacterial community composition, Bozena and Dudkowiak (2007) concluded that dredging operations reduce the capacity of an ecosystem to 'self purify' and increase the abundance of pathogenic bacteria.

This study examines growth and carbon metabolism of heterotrophic bacteria during three sampling events that bracket the August 2002-October 2003 dredging of the Ala Wai canal. Parameters selected for this survey focus on the capacity of this estuary to metabolize organic pollutants and POM prior to export to the Pacific Ocean. Growth of resident bacteria, also called heterotrophic production, was measured by ^{3}H-leucine uptake into proteins during growth of new bacterial biomass (Kirchman et al. 1985). Carbon metabolism in sediments was measured by ^{14}C-radiolabelled substrate mineralization (naphthalene, phenanthrene, fluoranthene, catechol, 2,4,6-trinitrotoluene) to $^{14}CO_2$ (Boyd, T.J. et al. 2005). In addition, sediment organic matter was analyzed for total lignin and specific lignin-derived

phenol concentrations. Concurrent water column physicochemical parameters were also measured (DO, pH, temperature, salinity).

Material and Methods:

Site The dredging operation was conducted from August 2002 to October 2003 (Table 1). Sampling stations extended from the Ala Wai Boat Harbor just outside the mouth of the Ala Wai canal (station 1) to the end of the canal towards Diamond Head (station 11; Figure 1). As part of the dredging operation, sediment was removed approximately from just inside the mouth of the canal (station 2) to past the mouth of the confluence with the Manoa-Palalo Drainage canal (station 7) and then from end of the canal (station 11; Figure 2).

Sediment sampling Three sampling events in the Ala Wai canal included the pre-dredge sampling from 18-20 June 2002 (11 stations), mid-dredge sampling from 19-21 February 2003 (6 stations), and post-dredge sampling from 2-4 December 2003 (10 stations; Table 1). The mid-dredge sampling was limited to 6 stations because of the presence of the dredge and silt curtains.

Heterotrophic bacterial production Bacterial production was measured using the leucine incorporation method (Kirchman et al. 1985, Kirchman 1993, Smith and Azam 1992) as adapted by Montgomery et al. (2008). Briefly, a 0.50 µL aliquot of wet sediment from each station was added to 2 mL microcentrifuge tubes (three experimental and one control) that were pre-charged with [^{3}H-4,5]-L-leucine (154 mCi mmol^{-1}). Sediment was extracted from a sediment core section or benthic grab sample and added to a microcentrifuge tube using a 1 mL plastic syringe with the end cut off. One mL of filtered bottom water (0.45 µm nom. pore dia.; Acrodisk, Gelman) that was collected <1 m above the sediment-water interface (SWI) was added to each tube and vortexed into a sediment slurry. Samples were incubated for 2 h at *in situ* temperatures and subsequently processed by the method above. For all samples, a constant isotope dilution factor (2.0) was used which was estimated from actual measurements of sediment dissolved free amino acids (Burdige and Martens 1990) and saturation experiment estimates (Tuominen 1995). One mL-syringed samples of wet sediment were dried (O/N, 50^{o}C) and values used to convert production to dry weight. Finally, incorporation rate of leucine into cellular macromolecules was applied to estimates of bacterial carbon production using conversion factors determined by Simon and Azam (1989).

PAH concentration Ambient PAH concentrations of 18 semivolatile priority pollutants were determined by mixing sediment (10-15 g wet weight) with diatomaceous earth prior to methanol extraction using accelerated solvent extraction. A 50:50 hexane:dichloromethane solvent mixture was used for extraction. Temperature was set at 100 °C, with pressure of 2400 PSI. Extraction was carried out for 20 minutes. Extracts were concentrated under a N_2 gas stream (Speedvap) prior to separation and analysis using gas chromatography/mass spectrometry (GC/MS) (Fisher et al. 1997) with p-Terphenyl-d^{14} and 2-fluorobiphenyl used as surrogate standards (Pohlman et al. 2002).

Carbon mineralization Carbon substrate mineralization assays were initiated within two hours of sediment sample collection using the method of Boyd, T.J. et al. (2005). Three sentinel PAHs: UL-^{14}C-naphthalene (specific activity: 18.6 mCi mmol^{-1}), 3-^{14}C-fluoranthene (45 mCi mmol^{-1}), and 9-^{14}C-phenanthrene (55 mCi mmol^{-1}) (Sigma Chemical), as well as the lignin degradation intermediate, UL-^{14}C-catechol (1.8 mCi mmol^{-1}, Sigma Chemical), and the energetic contaminant, UL-^{14}C-2,4,6-Trinitrotoluene

(TNT, 4 mCi $mmol^{-1}$; American Radiochemical Corporation) were used as radiotracers. Substrates were added in separate incubations to surface sediment and core section samples (1 mL wet volume) in 100 × 16 mm test tubes to a final concentration of about 0.2 μg g^{-1}. Filtered bottom water (0.5 mL) was added to each tube and vortexed to form slurry. For the three PAHs, isotope dilution was calculated from the ambient test PAH concentration and was kept under 10 % so that the system was not overwhelmed with excess PAH. Samples were incubated (24 h, *in situ* temperature) as evolved $^{14}CO_2$ was captured on NaOH-soaked filter papers. Incubations were ended by adding H_2SO_4 (2 mL, 2M) and to partition any remaining CO_2 into the headspace of the tube to the filter paper trap. A control for each sample was similarly treated except H_2SO_4 was added at T0 for each incubation. Filter paper traps containing metabolized $^{14}CO_2$ were removed and radioassayed prior to calculation of substrate mineralization rate.

Organic matter Total organic carbon (TOC) and nitrogen (TON) was measured in sediments by standard methods (UNESCO 1994) using a Carlo Erba Model 1108 Elemental Analyzer equipped with Eager 300 software and values presented in percent carbon on a dry weight basis. Acetanilide of known % C and % N was analyzed as a standard reference material.

Lignin Sediment lignin concentration was measured using an alkaline hydrolysis oxidation method to liberate lignin-derived methoxyphenols (LPs) derived from the parent lignin compound (Montgomery and Osburn 2003). LPs were subsequently derivatized with 1 % BSTFA to silyate exchangeable hydrogen, and subsequently analyzed using GC/MS (Goni and Montgomery 2000). LPs were separated after splitless, on-column injector with a flow rate of 1.3 mL min^{-1}, via a J&W Scientific DB-1 column (60 m × 0.32 mm i.d., 0.2 μm film thicknesses) with the following conditions: 100 °C initial temperature, 4 °C min^{-1} temperature ramp, 320 °C final temperature, and final hold of 10 min. Mass spectra of eluted peaks were acquired on an HP 6890/5973 GC/MS and identified and quantified using an internal laboratory library created based on retention times and m/z values for known standard LPs (Sigma-Aldrich). Total lignin concentration is given as the sum of the eight LPs per total dry weight (S8) or per 100 mg organic carbon (L).

Hydrodynamic data Vertical temperature, salinity, and salinity-corrected dissolved oxygen (DO) profiles were obtained at all stations using a Hydrolab™ integrated analysis system. Samples were collected at 0.1 m below the surface, 0.5 to 1 m above the bottom and at 1 m intervals between surface and bottom. Bottom water was collected simultaneously with a submersible impeller pump and hose system into acid washed, polypropylene bottles, which were rinsed three times with site water. Samples were held in the dark during transport and processed within two hours.

Meiofauna Benthic grab collected sediment was sampled using a hand-held piston corer (50 cc syringe; 6.2 cm^2). Samples were preserved in 70 % ethanol stained with rose bengal to facilitate sorting. Back in the laboratory, samples were sieved through a 53 μ mesh sieve previous to sorting under a dissecting scope. Animals were identified to major taxonomical levels (typically Order).

Results:

Heterotrophic bacterial production The rate of bacterial production in surface sediments increased at each station in the post-dredge sampling relative to the pre-dredge sampling, though stations 2 and 11 could not be compared directly (Figure 3). Pre-dredge surface sediment production ranged from 13±1.9 to 126±32 μg C kg^{-1} d^{-1} compared with the post-dredge sample range of 33±12 to 412±86.6 μg C

kg^{-1} d^{-1}. The mid-dredge surface sediments had the lowest values of the three samplings ranging from 0.0±2.1 to 23±2.3 μg C kg^{-1} d^{-1}. In general, bacterial production increased towards the mouth of the Ala Wai canal and was often lowest at stations 8 to 11 (Figure 3). There was a weak positive correlation (R^2 = 0.44) between bacterial production and bottom water dissolved oxygen concentration for the post-dredge sampling (Figure 4).

In depth profiles of 15-cm long cores from stations 5, 7, and 11 in the pre-dredge sampling, bacterial production decreased with depth to 6 cm below SWI (Figure 5). Production in deeper cores sections (6-15 cm below SWI) was near the method detection limit (1.0 μg C kg^{-1} d^{-1}). The mid-dredge cores from stations 1 and 5 had production values near the detection limit for all core sections (Figure 6). Production in cores from stations 2, 5, 7 after dredging decreased with depth (with the exception of the 12-15 cm section of station 2) and all values were well above the assay detection limit (Figure 7).

Carbon mineralization ^{14}C-labelled substrate conversion rate to $^{14}CO_2$ was used to estimate bacteria carbon metabolism rates for catechol, 2,4,6-trinitotoluene, phenanthrene, naphthalene and fluoranthene. Ambient catechol and 2,4,6-trinitotoluene concentration in the sediment were not measured but total PAH concentrations (including phenanthrene, naphthalene and fluoranthene) ranged from 0.20 to 7.0 ppm (Table 2). Catechol, phenanthrene, and fluoranthene mineralization was measured for sediments of all three samplings. Naphthalene mineralization was measured for the pre-dredge and mid-dredge samplings. 2,4,6-trinitrotoluene mineralization was only measured for the post-dredge sampling. In general, mineralization rate followed this pattern: catechol >> 2,4,6-trinitrotoluene > phenanthrene > naphthalene > fluoranthene.

Catechol is a relatively labile intermediate involved in lignin degradation and areas where lignin and other more refractory materials are being metabolized may have more rapid mineralization rates. Comparing all three samplings, catechol mineralization was more rapid in the surface sediment during the mid-dredge sampling at five of the six stations measured during all three samplings (1, 2, 3, 4, and 6; Figure 8). Catechol mineralization was higher in eight of ten post-dredge stations when compared with those same pre-dredge stations and ranged from below detection to 2040±1300 μg C kg^{-1} d^{-1} for all stations (Figure 8). When comparing profiles amongst the cores, there was little pattern with depth for either the pre-dredge (Figure 9), mid-dredge (Figure 10) or post-dredge cores (Figure 11).

Although not a common component of urban runoff, TNT is a contaminant associated with unexploded ordnance in some coastal waters of Oahu. As an aromatic organic carbon substrate, TNT may be rapidly metabolized by microbial assemblages adapted for degradation of other aromatics, such as lignin and PAH (Van Aken et al 1999, Kim and Song 2003, Peng et al. 2008). TNT mineralization rate in the Ala Wai canal sediment ranged from below detection to 17±2.7 μg C kg^{-1} d^{-1} in surface sediments of the post-dredge sampling and to 114±120 μg C kg^{-1} d^{-1} with depth in the three cores (Figure 12).

In general, phenanthrene mineralization rate was more rapid for surface sediments on the seaward side of the confluence with the Manoa canal (stations 1-7) and ranged from below detection at station 11 to 89±56 μg C kg^{-1} d^{-1} at station 1 at the Ala Wai mouth during the pre-dredge sampling (Figure 13). When comparing profiles among the cores, there was little pattern with depth for either the pre-dredge (Figure 14), mid-dredge (Figure 15) or post-dredge cores (Figure 16).

Naphthalene mineralization rate was not measured for the post-dredge sampling but ranged from 0.06±0.02 μg C kg^{-1} d^{-1} at station 11 of the pre-dredge sampling to 17±3.4 μg C kg^{-1} d^{-1} at station 5 of the mid-dredge sampling (Figure 17). There was not a pattern with depth for naphthalene mineralization in the three cores taken during the pre-dredge sampling (Figure 18), but was most rapid near the SWI (Figure 19).

Fluoranthene mineralization rate in surface sediments was least rapid of all the carbon substrates measured (ranging from non-detect (<0.01) to 3.0±1.3 μg C kg^{-1} d^{-1} and showed little pattern with distance from the ocean along the Ala Wai canal (Figure 20) or with depth for the pre-dredge (Figure 21), mid-dredge (Figure 22) or post-dredge cores (Figure 23).

Lignin Total lignin concentration is the sum of eight lignin-derived phenols: vanillin (Vl), acetovanillone (Vn), vanillic acid (Vd); which are synthesized in all vascular plants; syringealdehyde (Sl), acetosyringone (Sn), syringic acid (Sd), which are synthesized only in angiosperms; and, coumaric acid (pCd), ferulic acid (Fd), which are synthesized in nonwoody tissues (leaves, needles). The lowest total lignin concentrations (S8) were near the mouth of the Manoa-Palalo drainage canal (station 7) and the highest were near the Ala Wai mouth (stations 1-3) (Figure 24). The six syringyl and vanillyl phenols (L6) comprise the smallest portion of total organic carbon at station 7 and increase with distance in each direction away from this station in the Ala Wai (Figure 24).

Ratios of the lignin-derived phenols can be used to determine relative contributions of plant matter types to the sediment organic matter. Ratio of total syringyl to vanillyl phenols (S/V), was greater than 0.6 for all stations except station 4 (S/V=0.59), indicating angiosperms contribute most of the lignin-derived organic matter to the Ala Wai (Figure 25). Elevated ratio of cinnamyl to vanillyl phenols (C/V > 0.1) can indicate the presence of non-woody tissue such as leaves, needles, and grasses as cinnamyl phenols are only synthesized in these tissues. All stations had C/V ratios greater than 0.1 indicating much of the lignin-derived organic matter is likely from nonwoody tissue (Figure 25).

Lignin degradation in sediment has been measured using an index comprised of the ratio of acid to aldehyde for the vanillin family of lignin phenols ($[Ad/Al]_v$, Ertel et al. 1986; Dittmar and Lara 2001). Bacterial metabolism of lignin proceeds as aldehyde moieties are oxidized to acidic moieties that is reflected as an increase in $[Ad/Al]_v$ values in sediment organic matter. This ratio increased from the canal headwaters at station 10 to station 4 before decreasing again towards the canal mouth at station 2 (Figure 26) for the pre-dredge sampling. Catechol mineralization rate increased from the headwaters at station 10 to below the confluence with the Manoa (station 6) (Figure 26). Total lignin concentration is similar from station 4 to 10 before increasing at stations 2-3 near the canal mouth (Figure 26). Together this suggests that non-woody angiosperm plant matter (e.g. leaves, grasses) lignin inputs are initially deposited at the headwaters by station 10 and are then degraded as they migrate towards station 4. There may be either a new source of undegraded lignin, or depositional area for such material, near stations 2 of the canal, based on the S/V, C/V, and $[Ad/Al]_v$ ratios (Figures 25, 26).

Organic matter Carbon to nitrogen ratio (C/N) of organic matter in surface sediment ranged from 13 to 20 for pre-dredge samples (Figure 27) with the highest value at station 4, which was also the station with highest lignin concentration (Figure 26). Organic matter content ranged from 2.4 to 3.2 % for the pre-dredge sampling and 1.4 to 6.1 % for the post-dredge sampling (Figure 28). For the post-dredge

sampling, both the highest organic matter content and C/N ratio were at stations 3 and 7 (Figures 27 and 28).

Hydrodynamic parameters In the post-dredge sampling, water temperature at 2 m below the surface and 1 m above the SWI ranged from 25.9 to 26.5^{o}C. The surface water (0.1 m below surface) ranged from 23.9 and 26.2^{o}C and was between 0.3 and 2.6^{o}C cooler than bottom water (Figure 29). The greatest difference between surface water and middle or bottom water was at stations 6 and 7 and was likely the result on input from the Manoa canal (Figure 29). Likewise, the salinity stratification was most pronounced at where bottom salinity ranged from 32.5 to 34.4 PSU in middle and bottom sections of the water column and ranging from 10.6 to 28.3 PSU at the surface (Figure 30). Throughout the water column, pH was consistent, but generally decreased from the mouth of the Ala Wai canal (7.7-7.8 at station 1) to the headwaters (7.0-7.2 at station 10). The exception was the bottom water sample from station 7 which was the lowest of all bottom water stations (7.2) and may have been the result of surface sediment re-suspension during the sampling (Figure 31).

DO generally decreased (4.3 to <0.5 mg L^{-1}) with distance from the canal mouth in middle and bottom water (Figure 32). Surface water DO increased from 4.7 mg L^{-1} at the canal mouth to 5.8-6.0 mg L^{-1} at stations 4-6 before decreasing to 2.0 mg L^{-1} farther upstream of the sill created by the Manoa-Palalo Drainage Canal (stations 7-10) (Figure 32). It is important to note that DO measurements were made during daylight hours. Others (Laws et al. 1993) have reported DO super saturation in surface waters at these locations during the period of the day with highest solar flux, but that was not observed during this study.

Meiofauna Benthic meiofauna were identified to Order level and enumerated for surface grab samples for the predredge stations (June 2002). Several stations harbored few, if any, meiofauna (stations 2, 3, 5, 8, 9; Table 3). Station 4, which is in the small basic near the Makiki Stream outfall, had the greatest abundance and diversity of meiofauna. The most abundant group were the harpacticoid copepods (44), polychaetes (mostly larva, 37), nematodes (28), along with a few foraminiferans (4) and ostracods (33).

Discussion:

Because this paper is the first to report of bacterial production rates for the Ala Wai Canal water or sediments for context, rates observed during this study were compared with observations made in coastal Hawaiian waters (Table 4). The range of rates observed during the pre-dredge sampling (13-126 μg C kg^{-1} d^{-1}) is similar to that measured in Kahana Bay (42-121 μg C kg^{-1} d^{-1}) during the same period of the year (Montgomery et al. 2010). The range for the December post-dredge sediment sampling (33-412 μg C kg^{-1} d^{-1}) was higher than found for Pearl Harbor surface sediments at the same time of the year (23-38 μg C kg^{-1} d^{-1}, Montgomery and Osburn 2004).

In general, bacterial production in surface sediment increased three- to four fold towards the mouth of the Ala Wai canal and was often lowest at stations 8 to 11. This is the opposite trend of that reported for primary production which was highest at these terminal stations and decreased three- to four-fold towards the mouth from 675 to 3000 μg C L^{-1} d^{-1} (Harris 1975, Laws et al. 1993). This range of primary production is similar to that reported for nearby Mamala Bay (1900-4600 μg C L^{-1} d^{-1}) (Walker et al. 2006). High autochthonous organic input to sediments from phytoplankton biomass, allochthonous POM from surface runoff, as well as elevated nutrient input to the canal may stimulate heterotrophic production

in the water column. Laws et al. (1993) estimates that 70 % of POM input to the Ala Wai canal is respired by phytoplankton and heterotrophic bacte rioplankton resulting in DO depletion in bottom waters. Though there are no reports of heterotrophic production measurements for the Ala Wai canal water column, Laws et al. (1993) measured total respiration (2400-2850 μg C L^{-1} d^{-1}) which was two- to three orders of magnitude higher than that reported for heterotrophic bacterial production in nearby waters (Table 4). Elevated water column respiration rates, such as those reported by Laws et al. (1993), alone can result in significant depletion of DO and if coupled with limited reoxygenation of bottom waters through physical processes, periods of anoxia in the terminal basin may result (Laws et al. 1993). Anoxia may reduce heterotrophic bacterial production in bottom water and sediment. This may explain the observed decline in bacterial production with distance from the canal mouth. This hypothesis is supported by the observed positive correlation (R^2 = 0.44) between bacterial production and bottom DO during the post-dredge sampling. In addition, heterotrophic production increased at each station in the post-dredge (relative to the pre-dredge) sampling, presumably as water circulation increased in the waterway.

Organic carbon that is not respired in the water column eventually is exported from the canal to the Mamala Bay or settles in the surface sediment. POM metabolism in surface sediment can be enhanced by tidal pumping of oxygenated bottom waters and reworking of sediments by benthic infauna (Montgomery et al. 2008). One standard measure of bacterial carbon metabolism involves determining mineralization rates of ^{14}C-radiolabelled substrates to $^{14}CO_2$ (Deming 1993). Catechol mineralization rates were about an order of magnitude higher than heterotrophic production in the surface sediment, while TNT, phenanthrene and naphthalene mineralization rates were about the same order of magnitude and those for fluoranthene were an order of magnitude less rapid. Catechol mineralization was higher in eight of ten post-dredge stations when compared with those same pre-dredge stations suggesting that features of the dredging operation may have enhanced the capacity of the sediment assemblage to metabolize aromatic carbon substrates like lignin. Both catechol and phenanthrene mineralization rate were more rapid on the seaward side of the confluence with the Manoa-Palalo Drainage Canal though this may have been some function of higher bacterial production or DO concentration in the bottom water. Another reason for the relative differences in mineralization rates may be due to different incorporation efficiencies of the various substrate carbon sources into new bacterial biomass.

The range of catechol mineralization rates in the surface sediment of the Ala Wai canal was greater than that reported for Pearl Harbor (Montgomery and Osburn 2004) in the only comparable measurements for coastal Hawaiian waters (Table 5). TNT mineralization (ND-17 μg C kg^{-1} d^{-1}) was lower than that reported for Pearl Harbor (3-33 μg C kg^{-1} d^{-1}, Montgomery and Osburn 2004) or Kahana Bay (8-50 μg C kg^{-1} d^{-1}, Montgomery et al. 2010) (Table 5). Both Pearl Harbor and Kahana Bay are composed primarily of high salinity marine derived water with little freshwater input. Such locations are typically N-limited. Because the Ala Wai Canal receives proportionally more urban runoff (e.g., fertilizer) and freshwater, it follows that N-limitation is suppressed in the Ala Wai Canal and that metabolism of this N-containing aromatic may be lower as well. PAH mineralization rates were generally higher than those reported for sediments near the middle of Pearl Harbor (Montgomery and Osburn 2004) but lower than those taken near creosote-treated pilings (Boyd et al. 2008).

Lignin phenol analyses of the sediment organic matter suggest that non-woody angiosperm plant matter (e.g. leaves, grasses) is initially deposited at the canal headwaters and is then degraded as this material migrates toward the Mamala Bay. Prior to this report, the sediment organic matter was characterized

primarily by carbon and nitrogen content (Laws et al. 1993, Glenn et al. 1995, McMurtry et al. 1995) which provides limited information on source of the material. Organic matter content of surface sediment ranged from 2.4 to 3.2 % for the pre-dredge sampling and was much more variable (1.4-6.1 %) for the post-dredge sampling with the higher values similar to the 4 to 6 % reported by Glenn et al. (1995). Similarly, C/N ratios, which may distinguish OM source, did not suggest substantial change in source along the Ala Wai Canal, rather a slight increase in C/N ratio. These C/N values generally reflect terrestrial OM inputs (>>20) mixed in approximately equal proportion to phytoplankton (6-8; Meyers 1994) at Station 10 and increasing slightly (toward more terrestrial influence) at Station 2. No change in C/N from dredging is apparent (Figure 27). Lignin concentrations show a similar pattern, reflecting a larger contribution of these terrestrial biomarkers per gram dry weight down stream toward the mouth of the Ala Wai Canal. The dramatic drop in $[Ad/Al]_v$ just past the sill, coupled with a decrease in the S8 value suggests that the mouth of the Ala Wai is a site of OM accumulation of less-degraded material. Deposition of this organic matter, especially by the confluence with the Manoa, alters the bathymetry of the canal and contributes to reduced water circulation and increased vertical stratification (Glenn and McMurtry 1995).

During this study, the water column was vertically stratified with respect to salinity, DO, and temperature and horizontally stratified with respect to pH and DO. The most pronounced vertical gradients for salinity, DO and temperature were observed at stations 6 and 7 where the greatest input of freshwater drainage from the Manoa-Palalo Canal is observed. The salinity range for bottom water is similar to the 33-34 PSU reported by Laws et al. (1993) while the surface water range is well within the 0-32 PSU range reported by Gonzalez (1971). Glenn et al. (1995) reported higher salinity in the surface water of the terminal basin (28-32 vs. 26-28 PSU), but this may be due to the rainfall event that preceded the post-dredge sampling. In addition, surface water was between 0.3 and 2.6^{o}C cooler than bottom waters, which is a greater range than the 1^{o}C reported by Glenn et al. (1995) but lower than the 6^{o}C reported by Gonzalez (1971). Glenn et al. (1995) attributed these temperature differences to the lack of seaward transport of heat from the basin. DO generally decreased (4.3 to below 0.5 mg L^{-1}) with distance from the canal mouth in middle and bottom water and decreased with depth, especially in the terminal basin, as was reported by Laws et al. (1993). However, the highest DO concentrations were lower than the daytime concentrations of 6 to 9.5 mg L^{-1} reported by Laws et al. (1993). The pH of all three portions of the water column tended to be similar at a given station but generally decreased from the mouth of the Ala Wai canal (7.7-7.8 at station 1) to the headwaters (7.0-7.2 at station 10). Though pH may have a significant effect on nutrient and metal cycling in the Ala Wai, these appear to be the first reported values in the literature.

Vertical stratification and reduced oxygen concentration in bottom waters can limit abundance and diversity of benthic infauna in the Ala Wai canal (De Carlo and Anthony 2002, Resig et al. 1995). Reduced infaunal activity can inhibit biological mixing of surface sediment (bioturbation), which may promote the development of anoxia thus further lowering the capacity of the aerobic benthic community to metabolize organic contaminants (Montgomery et al. 2008). Overall, diversity and abundance of benthic meiofauna was low despite the reported high primary production in the overlying water column. The greatest meiofaunal diversity and abundance in this study was at station 4, which was nearest the Makiki Stream outfall. In a comprehensive study of foraminifera, Resig et al. (1995) found that diversity was highest near the mouth of the canal (station 2) and then decreased up the canal. High abundance

(though low diversity) found in the terminal basin was attributed to high primary production (and consequent anoxic bottom water) in that portion of the canal (Resig et al. 1995).

Because of the amplitude in changes in water flow, stratification, and oxygenation associated with high but episodic input of rainfall to the canal, it is not possible to solely attribute the post-dredge increase in bacterial production in surface sediment to dredging activity. However, a change in the relative distribution of OM types along the canal surface sediment was evident during this study. Pre-dredge samples had OM concentration in the relatively narrow range of 2.4-3.2 %, whereas after the dredging, some stations were accumulating OM to a much higher degree (1.4 % for station 4, 6.1 % for station 3), though this latter range was still within that found in previous investigations (Glenn et al. 1995). Additionally, while PAH mineralization was relatively low compared with other urbanized watersheds (Boyd et al. 2008), it may be because PAH inputs to the canal are low relative to the other OM sources (e.g., terrigenous plant matter, phytoplankton biomass). Even with enhanced flow associated with the dredging operation, it is probably unlikely that significant amounts of PAHs are being exported from the canal to the adjacent coastal waters.

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Table 1. Three sampling events performed in the Ala Wai canal from June 2002 to December 2003.

Event	Date	Stations
Pre-dredge sampling	18-20 June 2002	11
Dredge start	August 2002	---
Mid-dredge sampling	19-21 February 2003	6
Dredge end	October 2003	---
Post-dredge sampling	2-4 December 2003	10

Figure 1. Eleven stations (●) sampled in the Ala Wai Canal during three sampling events in June 2002, July 2003 and December 2003.

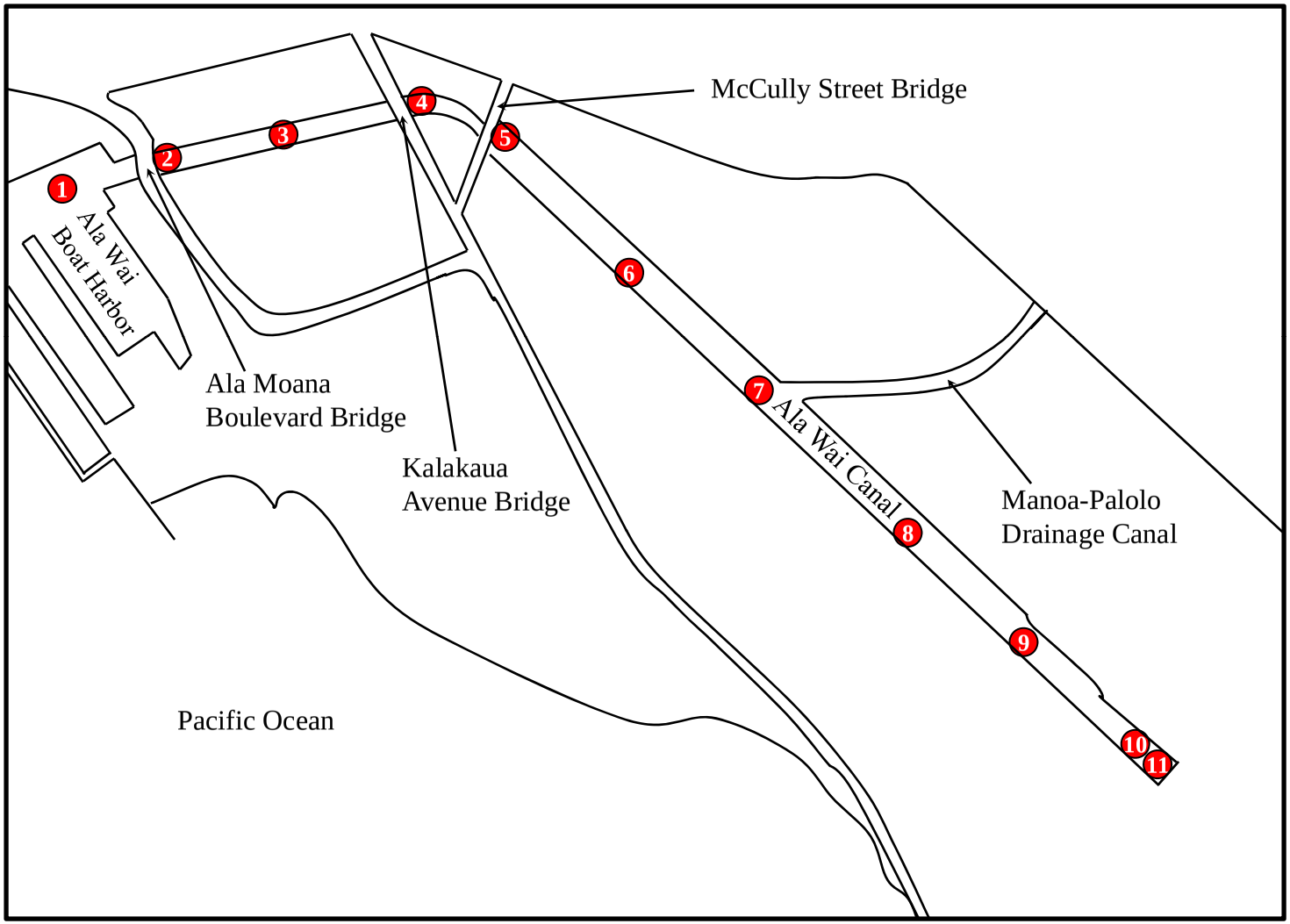

Figure 2. The schematic centerline profile with predredge depth (- - -) and the expected post-dredge depth (—) with eleven sampling stations in the Ala Wai Canal.

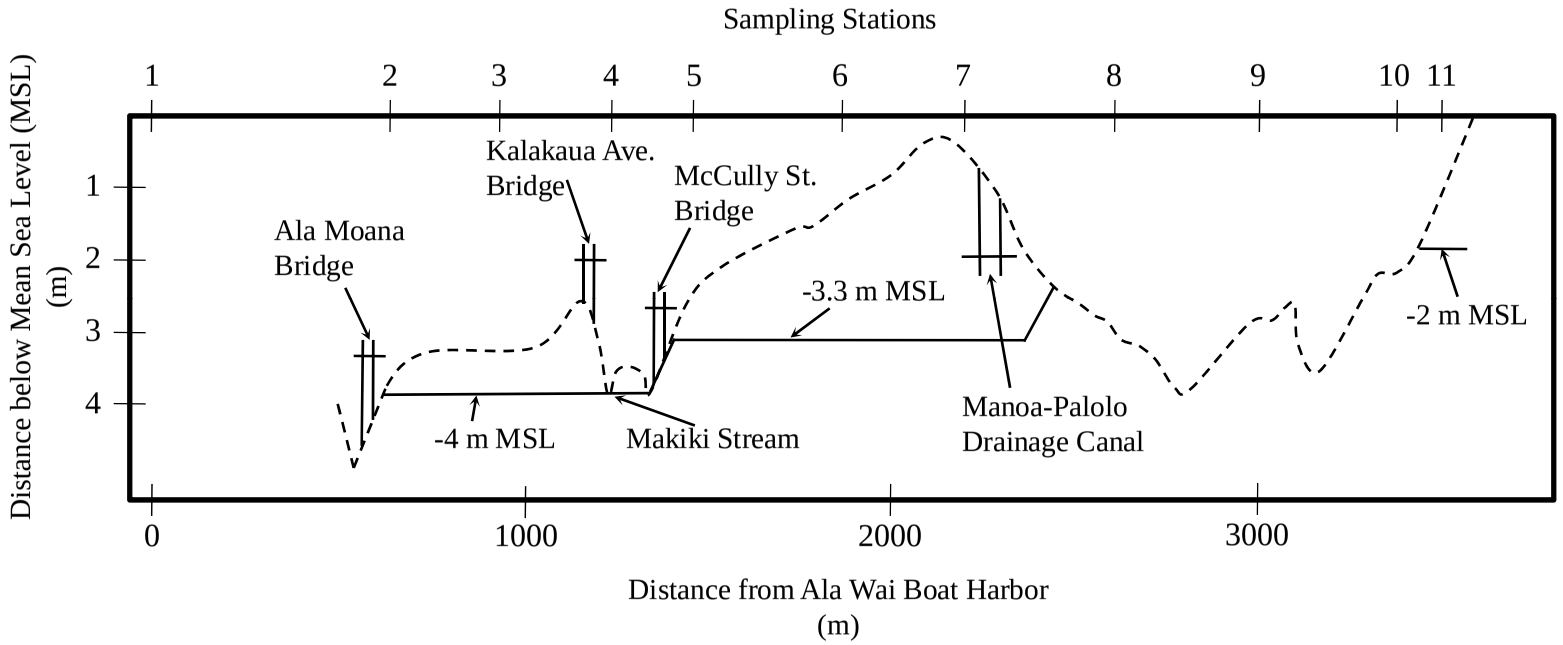

Figure 3. Bacterial production (μg C kg^{-1} d^{-1}) in surface sediments for three samplings with distance from the Ala Wai Boat Harbor (m).

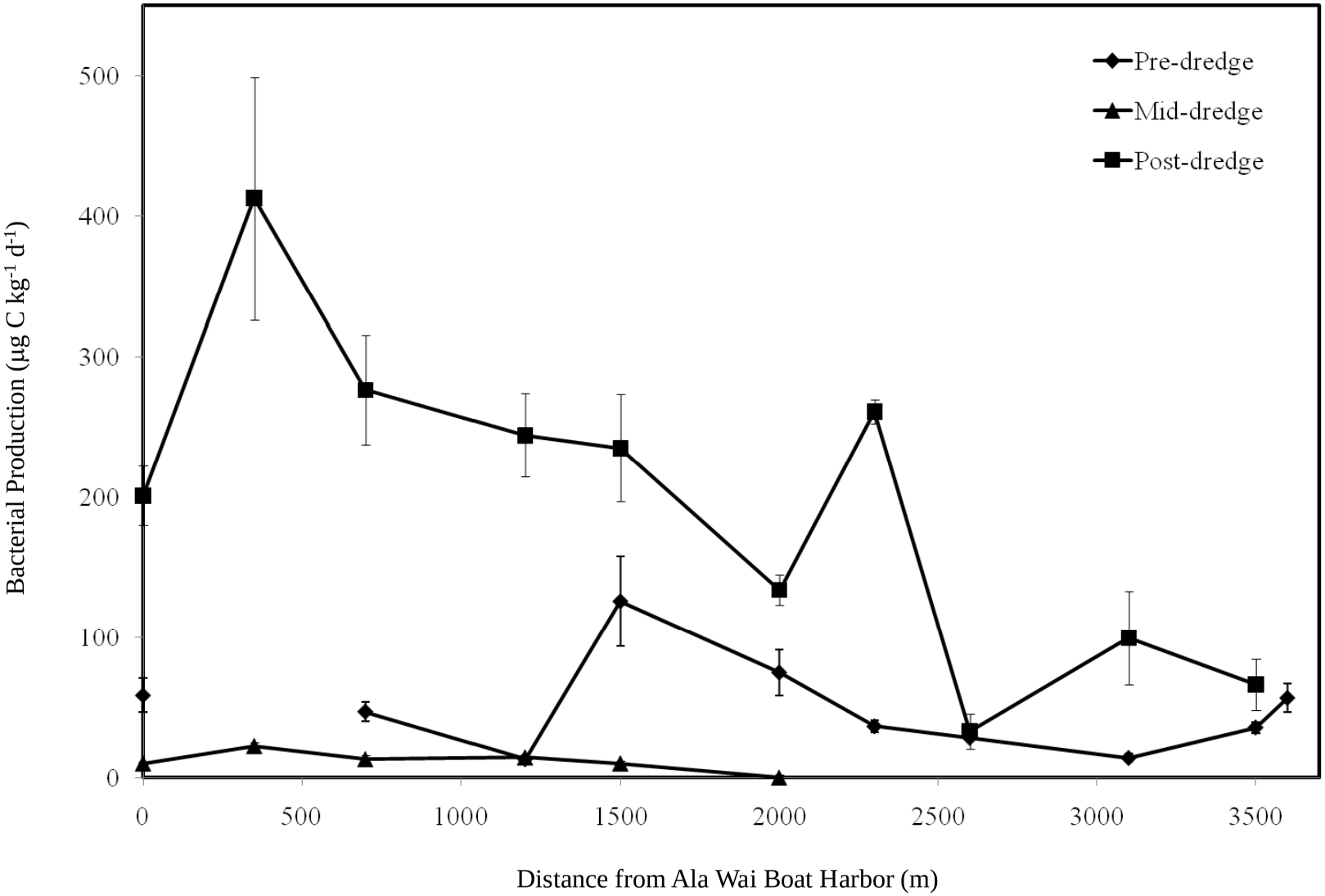

Figure 4. Bacterial production (μg C kg^{-1} d^{-1}) of surface sediment (post-dredge December 2003 sampling) increased with concentration of dissolved O_2 (mg L^{-1}) in the overlying bottom water.

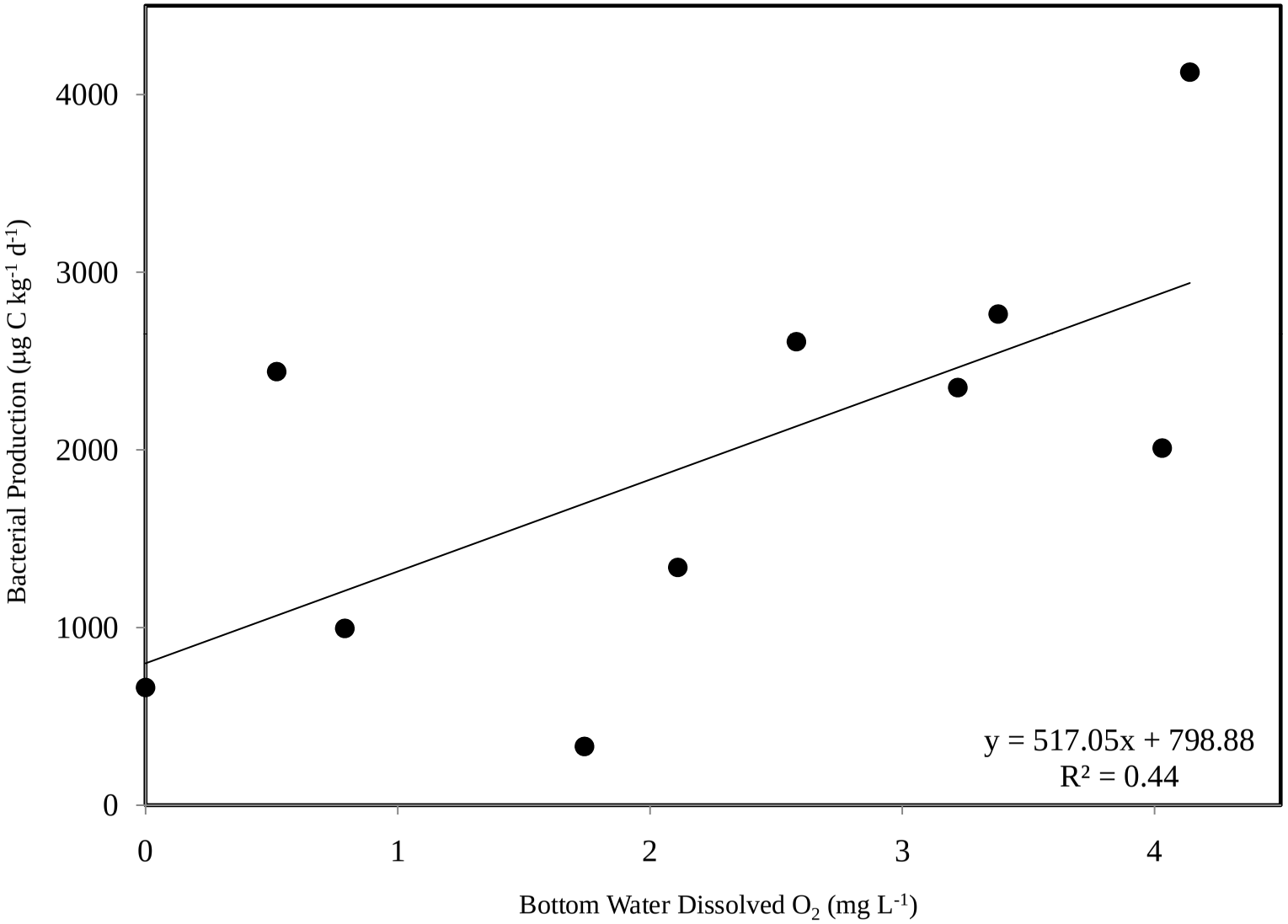

Figure 5. Bacterial production (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the pre-dredge June 2002 sampling.

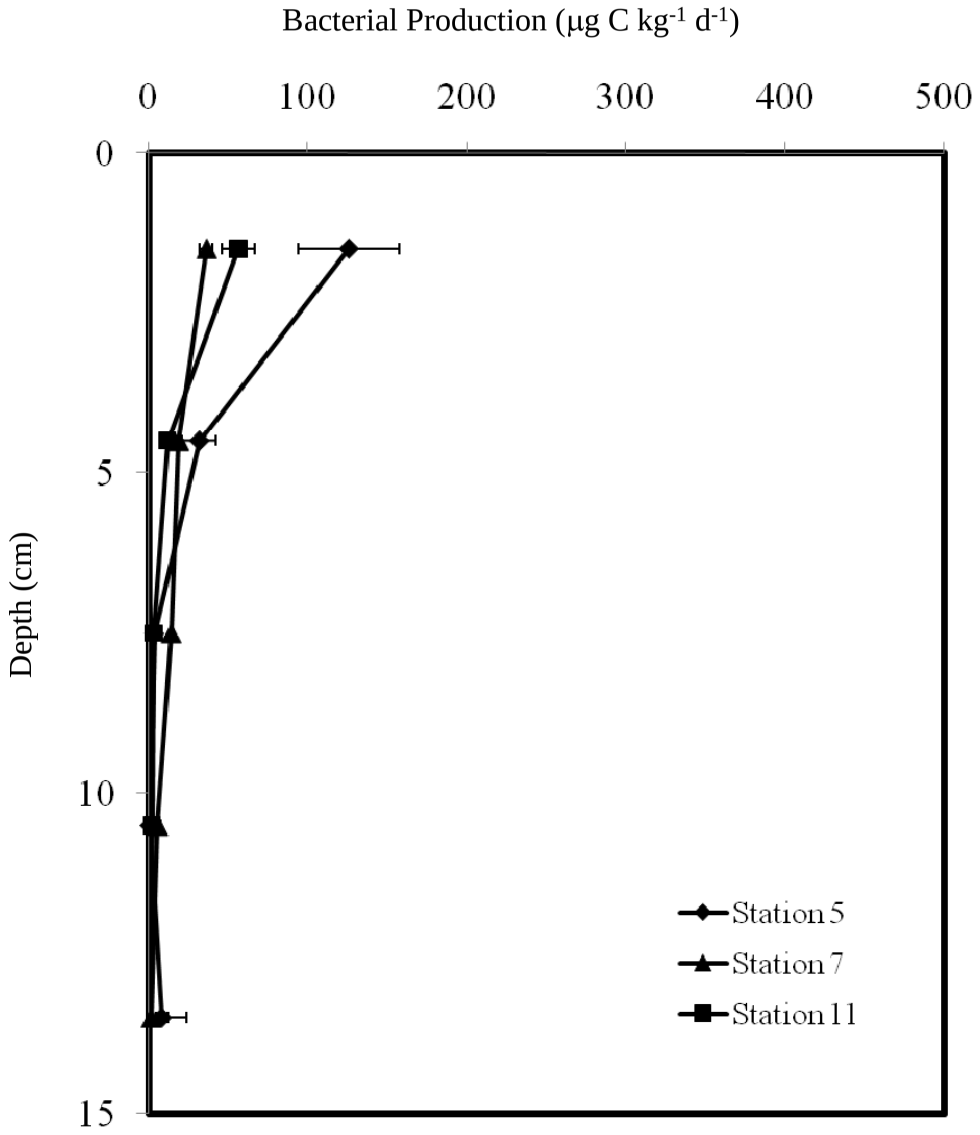

Figure 6. Bacterial production (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for two cores taken during the mid-dredge February 2003 sampling.

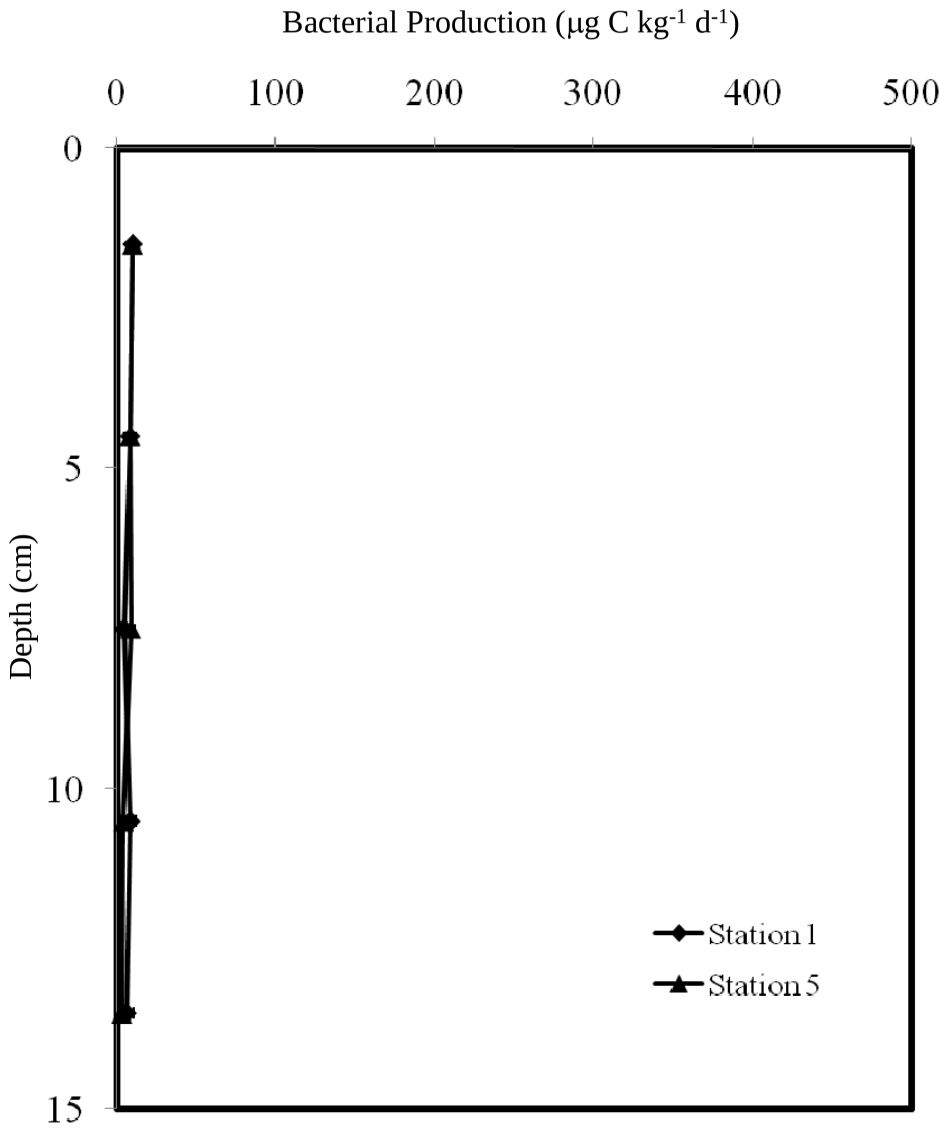

Figure 7. Bacterial production (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the post-dredge December 2003 sampling.

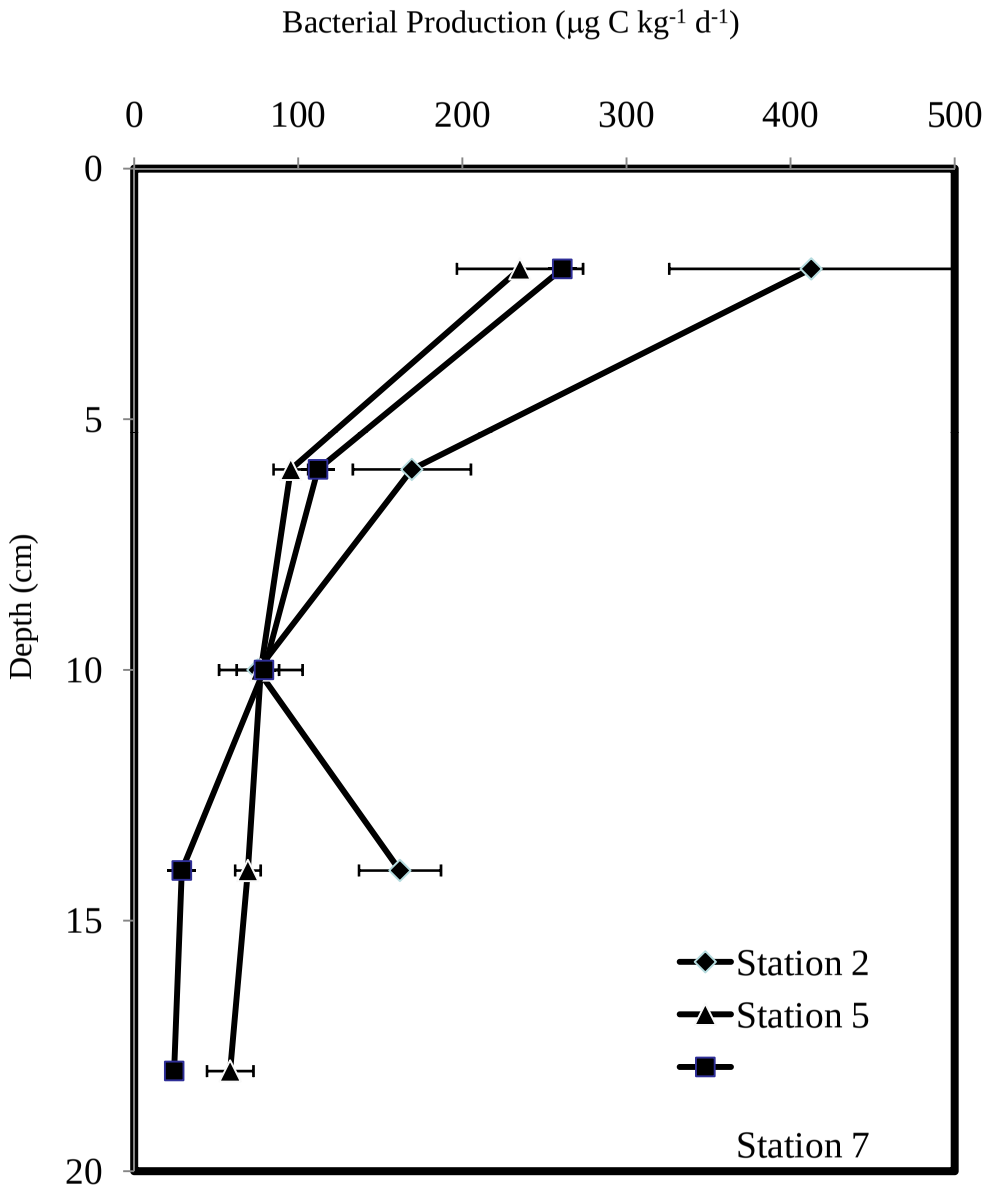

Table 2. PAH concentrations (ppm) for sediment from the pre-dredge samples (June 2002).

Station	**PAH Concentration** (ppm)				
	0-3 cm	3-6 cm	6-9 cm	9-12 cm	12-15 cm
1	0.30	---	---	---	---
2	0.62	---	---	---	---
3	2.6	---	---	---	---
4	7.0	---	---	---	---
5	1.3	0.81	1.4	0.34	1.33
6	2.2	---	---	---	---
7	0.81	0.61	0.49	0.20	0.29
8	2.2	---	---	---	---
9	2.5	---	---	---	---
10	3.9	---	---	---	---
11	4.9	4.7	5.2	5.5	5.0

Figure 8. Catechol mineralization rate (μg C kg^{-1} d^{-1}) in surface sediments for three samplings with distance from the Ala Wai Boat Harbor (m).

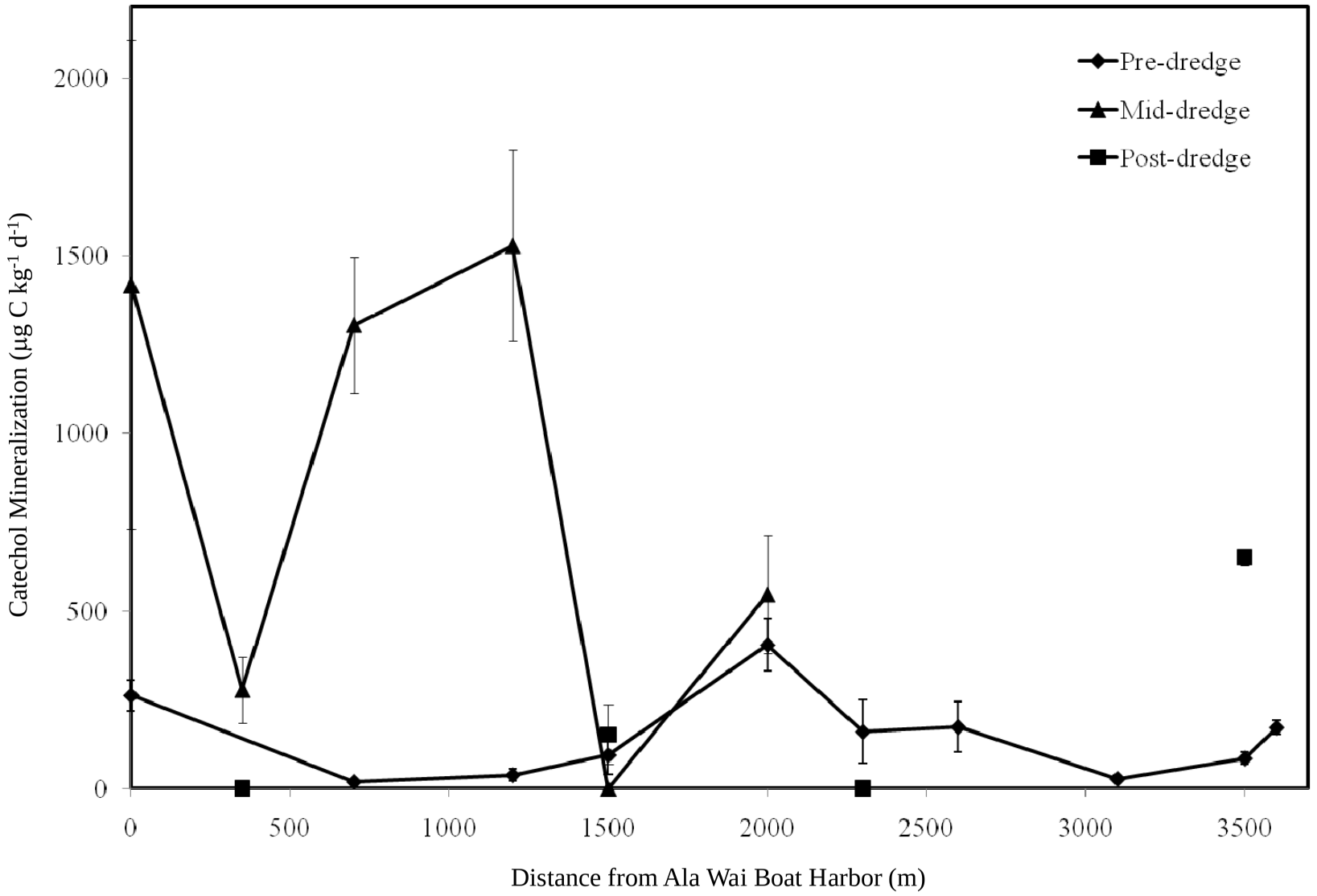

Figure 9. Catechol mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the pre-dredge June 2002 sampling.

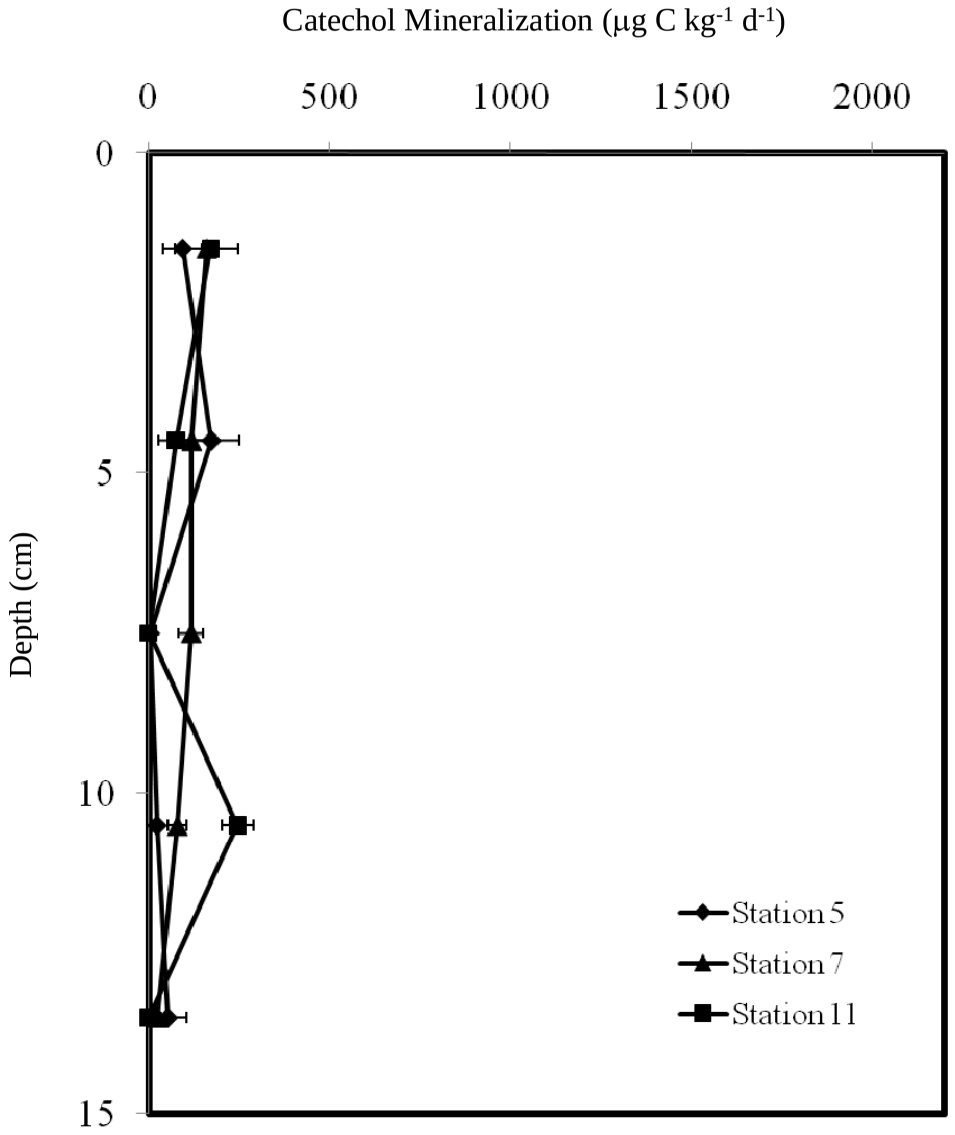

Figure 10. Catechol mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for two cores taken during the mid-dredge February 2003 sampling.

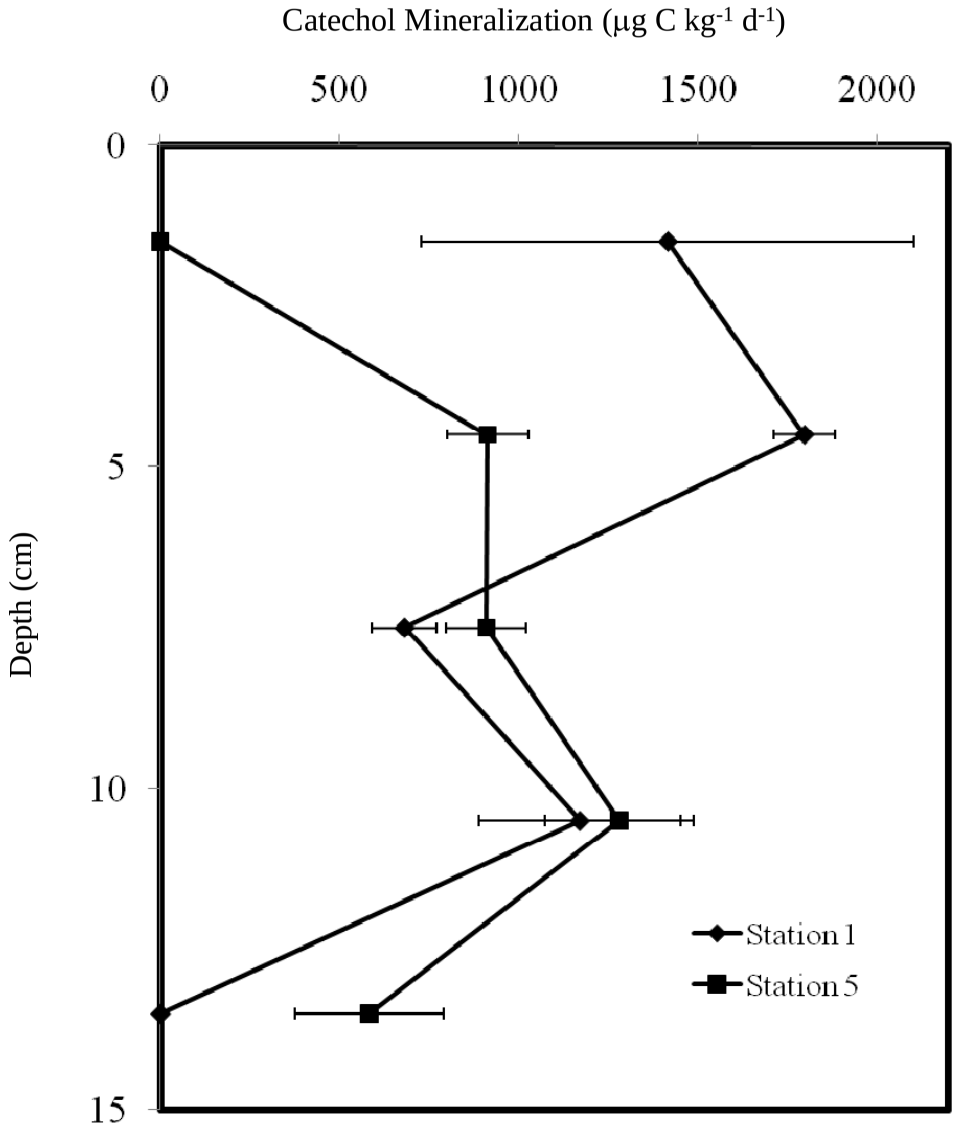

Figure 11. Catechol mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the post-dredge December 2003 sampling.

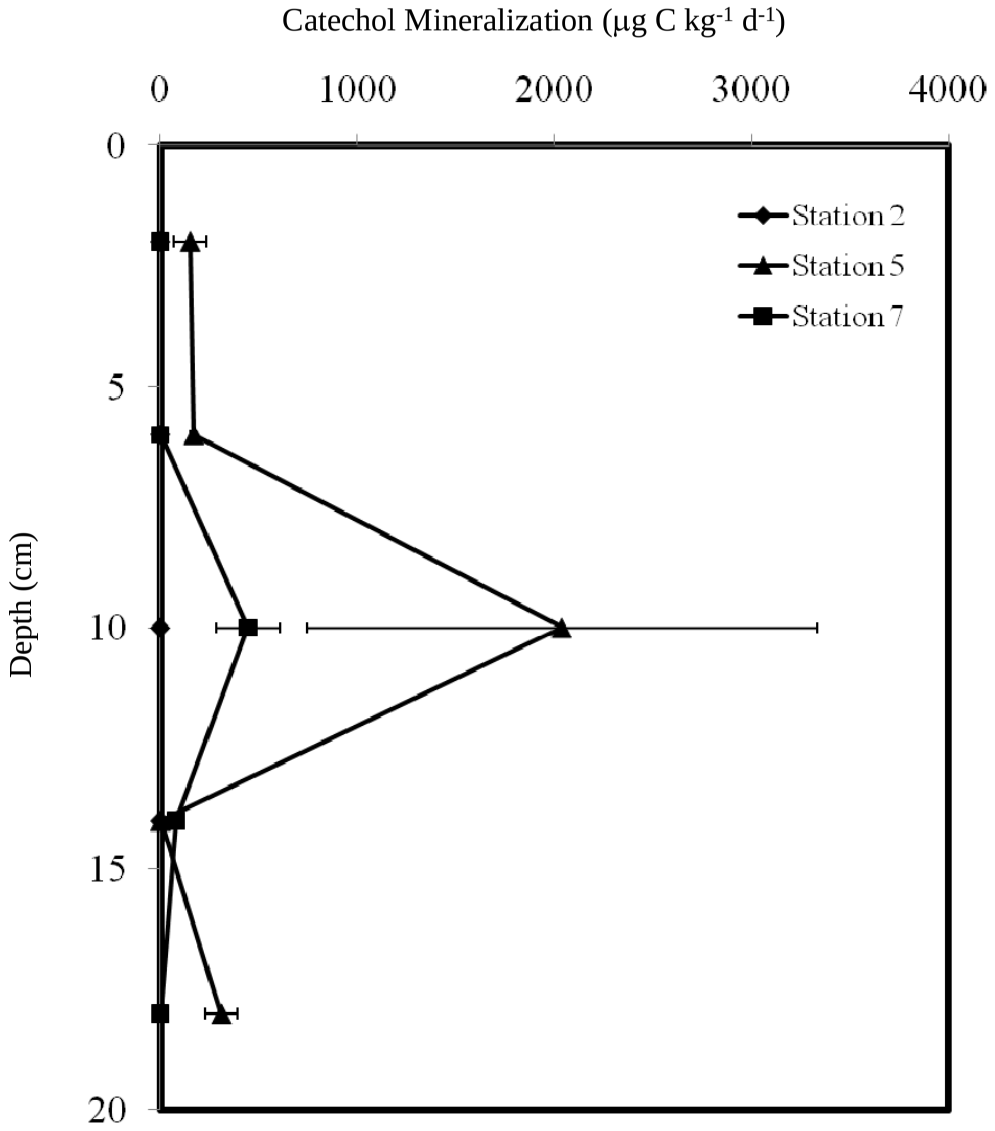

Figure 12. 2,4,6-Trinitrotoluene mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the post-dredge December 2003 sampling.

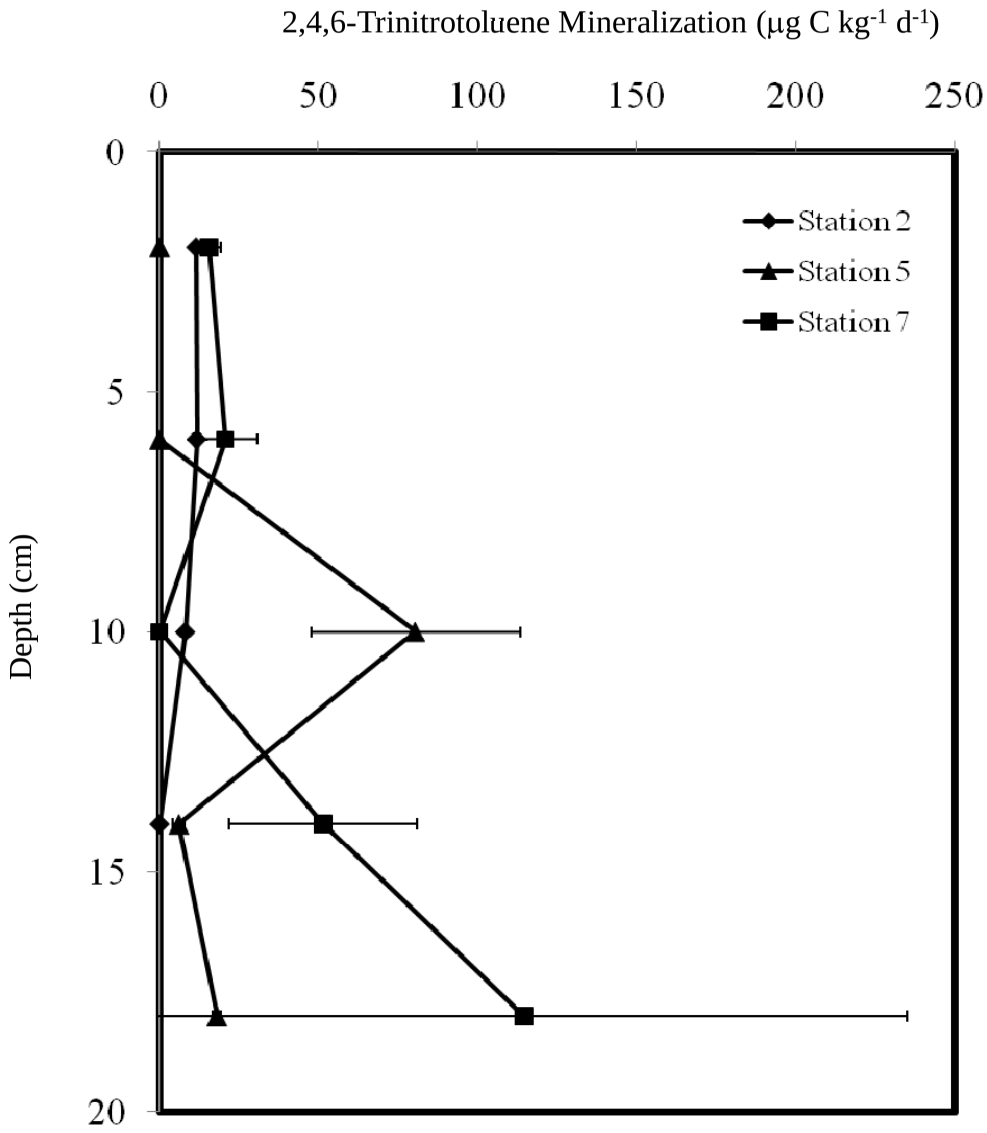

Figure 13. Phenanthrene mineralization rate (µg C kg^{-1} d^{-1}) in surface sediments for three samplings with distance from the Ala Wai Boat Harbor (m).

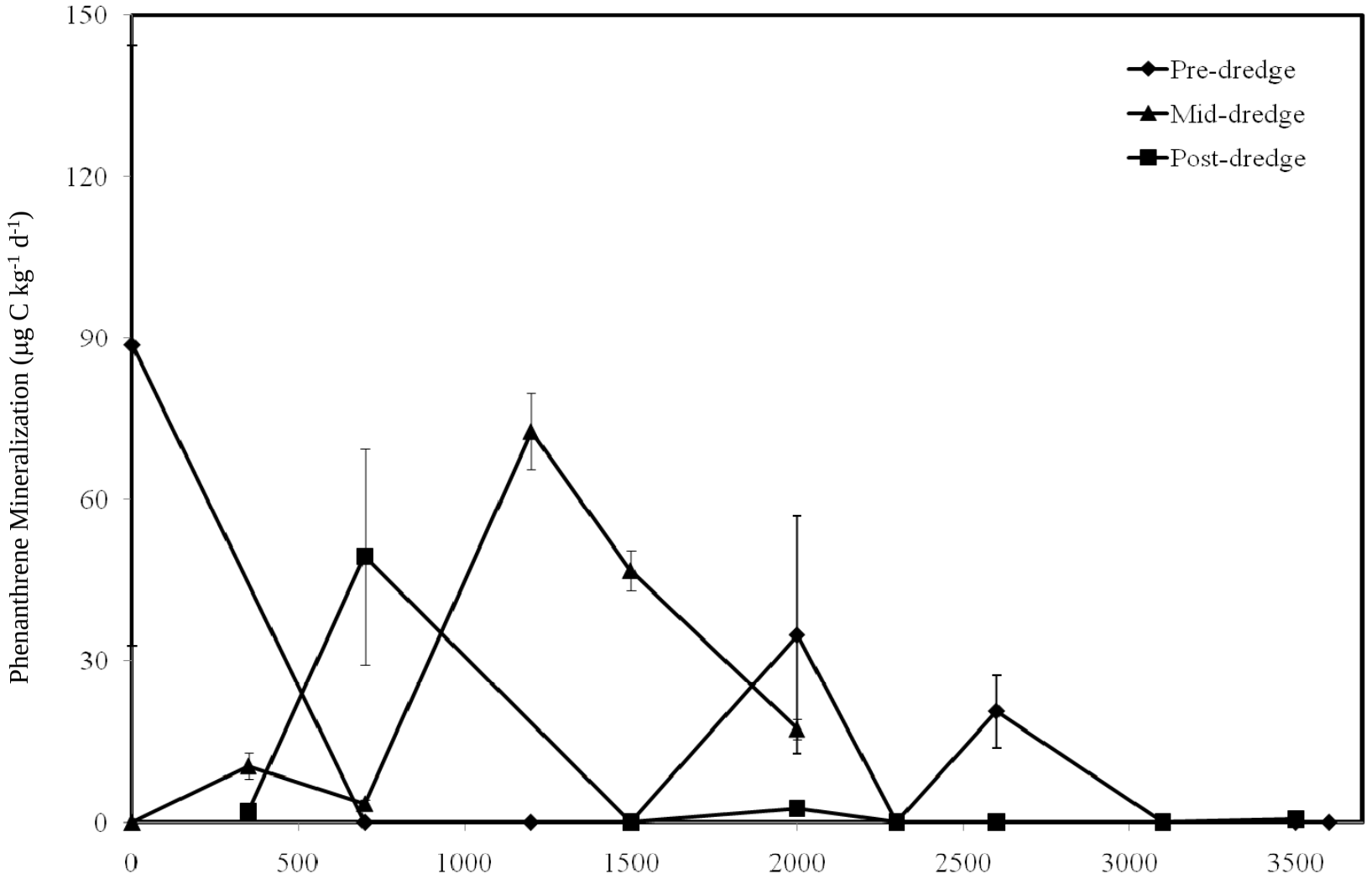

Figure 14. Phenanthrene mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the pre-dredge June 2002 sampling.

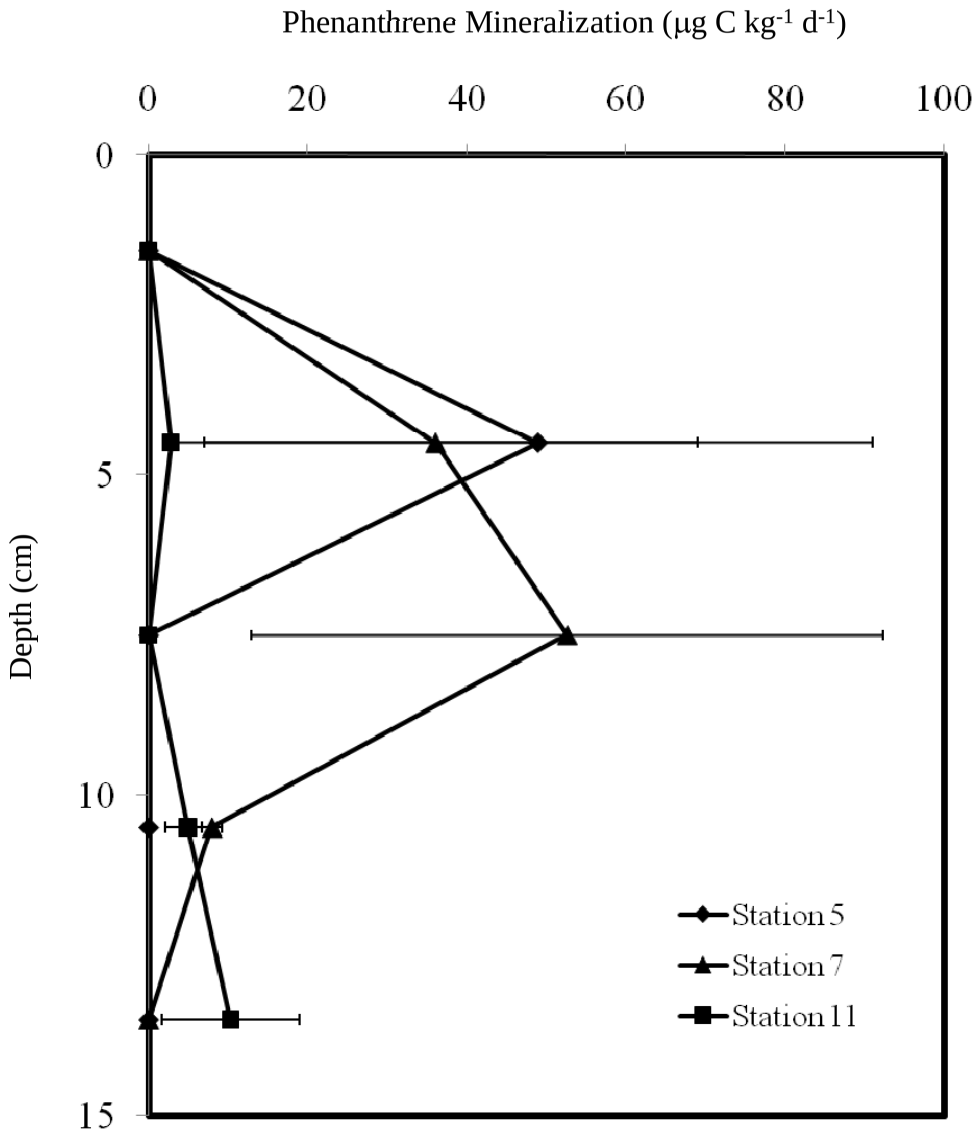

Figure 15. Phenanthrene mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for two cores taken during the mid-dredge February 2003 sampling.

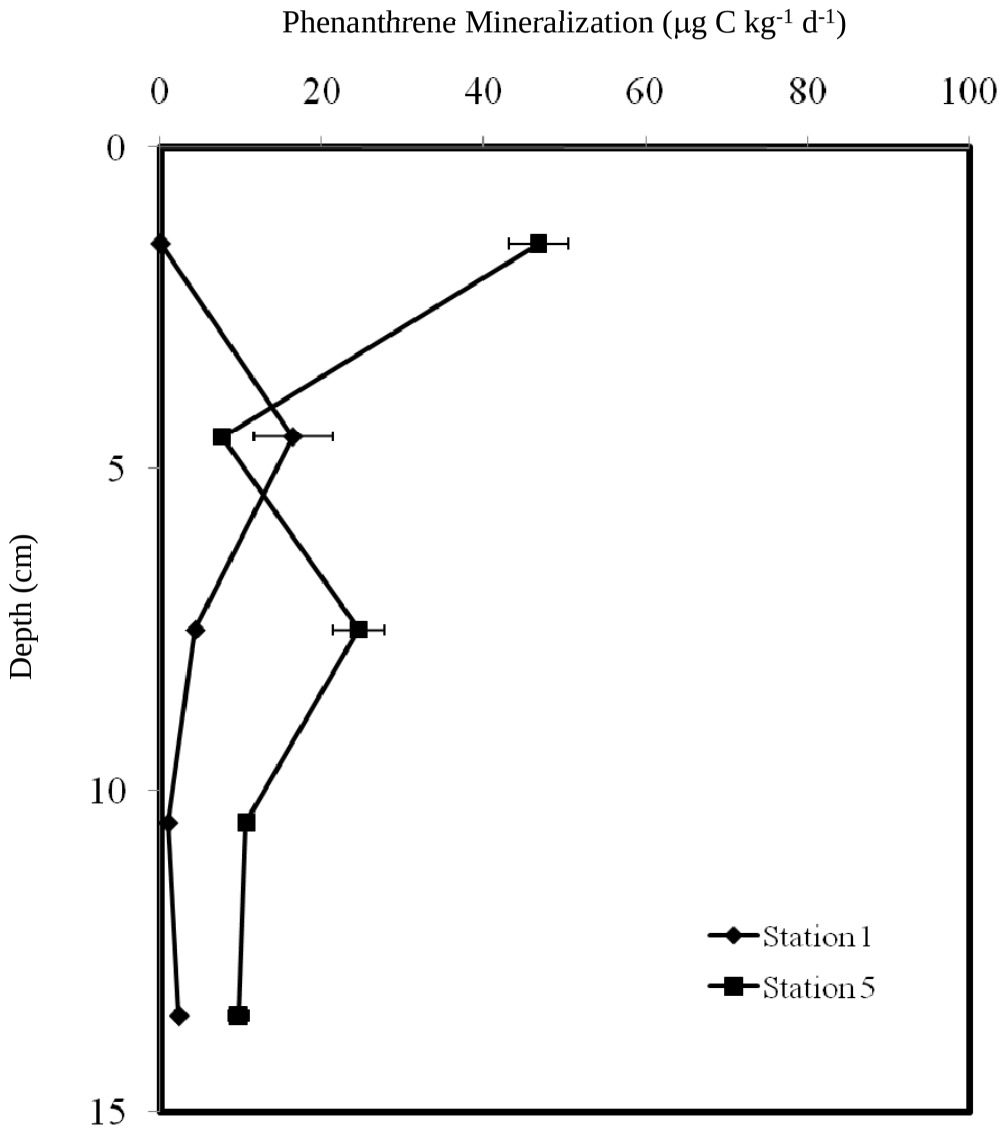

Figure 16. Phenanthrene mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the post-dredge December 2003 sampling.

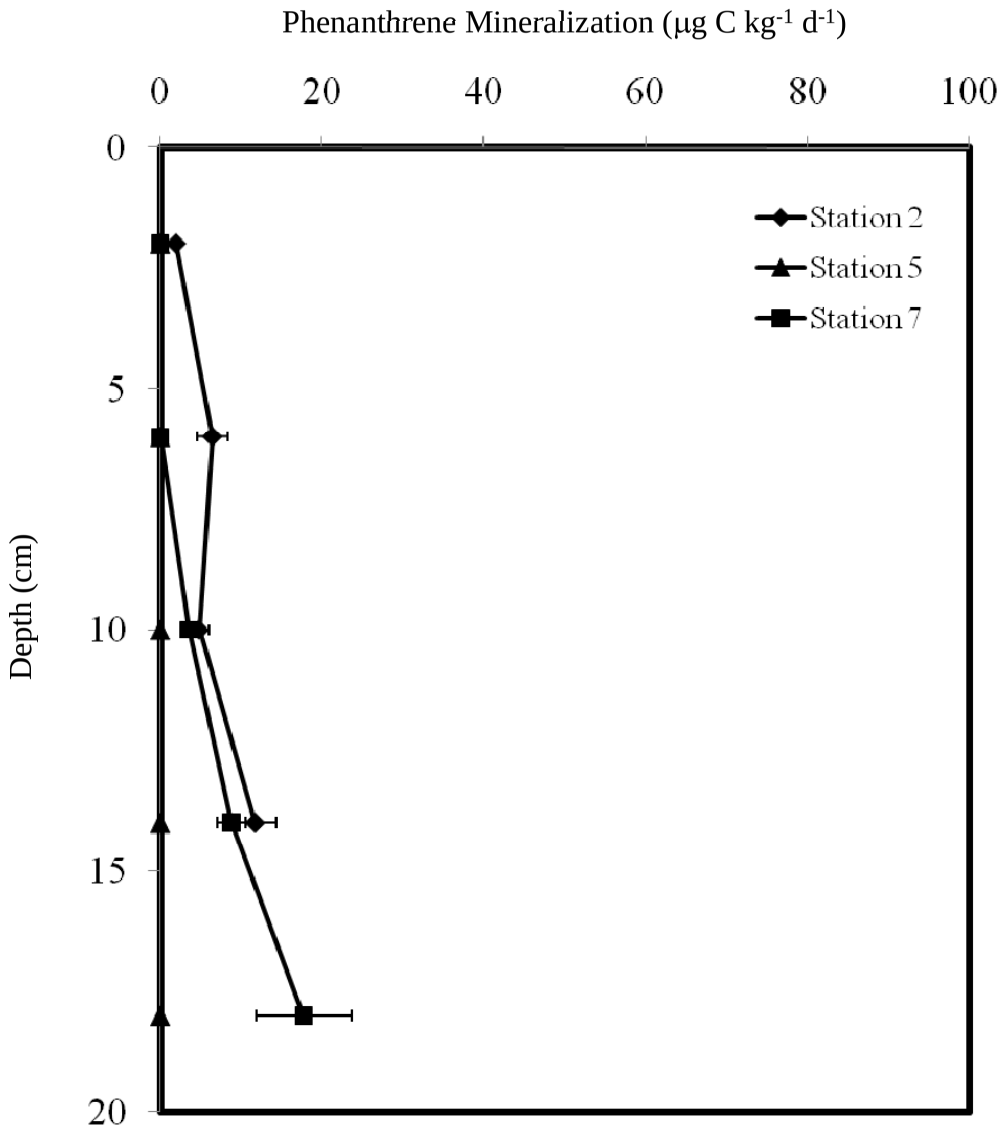

Figure 17. Naphthalene mineralization rate (μg C kg^{-1} d^{-1}) in surface sediments for three samplings with distance from the Ala Wai Boat Harbor (m).

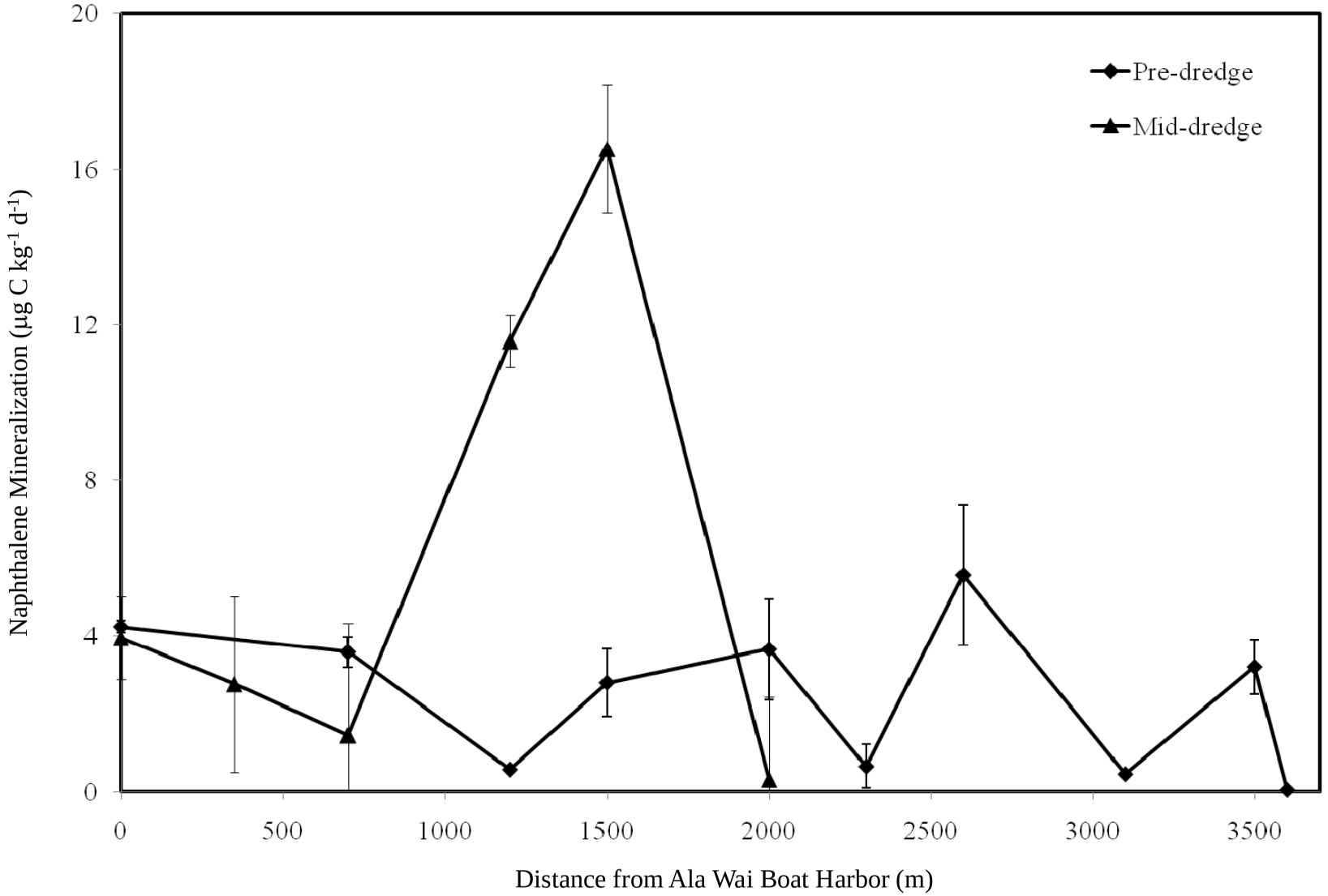

Figure 18. Naphthalene mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the pre-dredge June 2002 sampling.

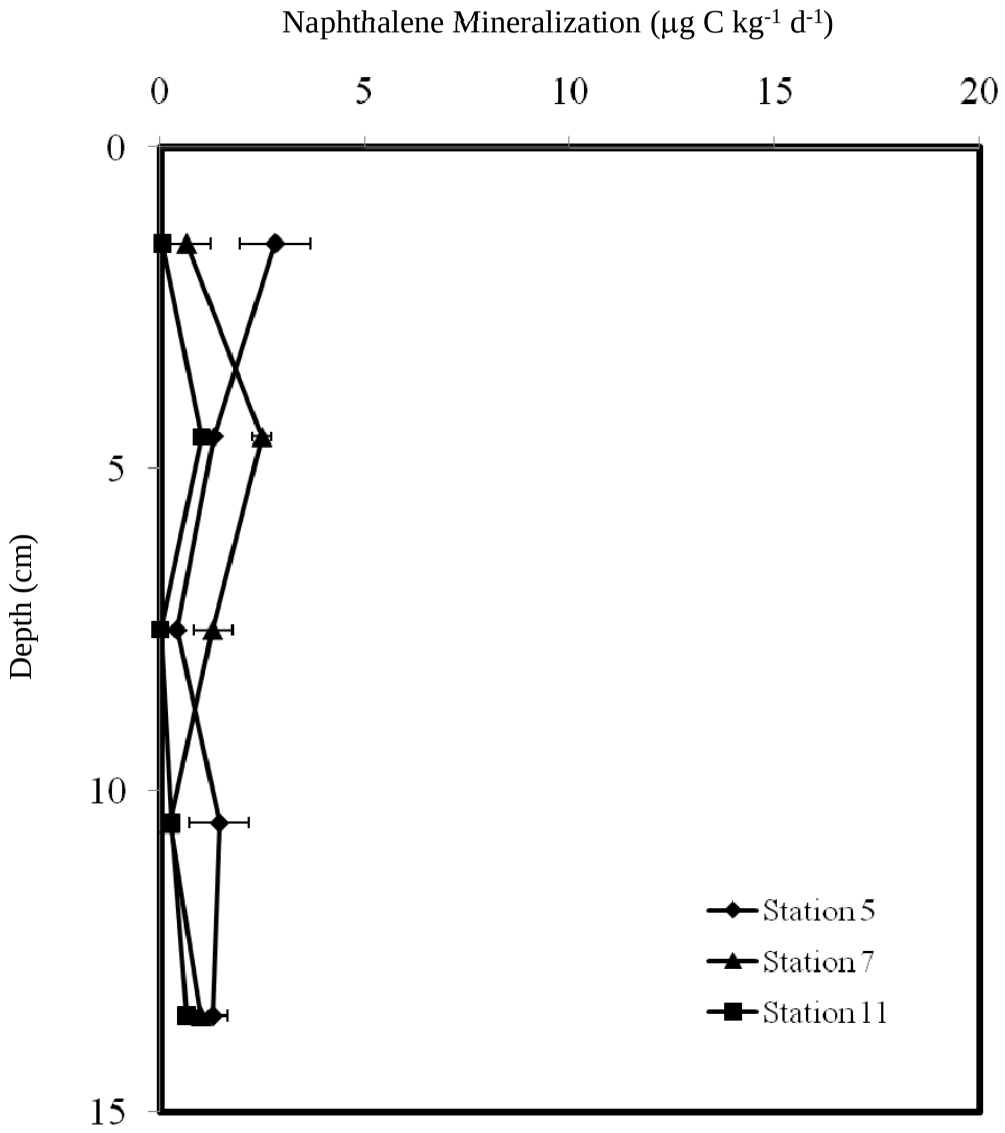

Figure 19. Naphthalene mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for two cores taken during the mid-dredge February 2003 sampling.

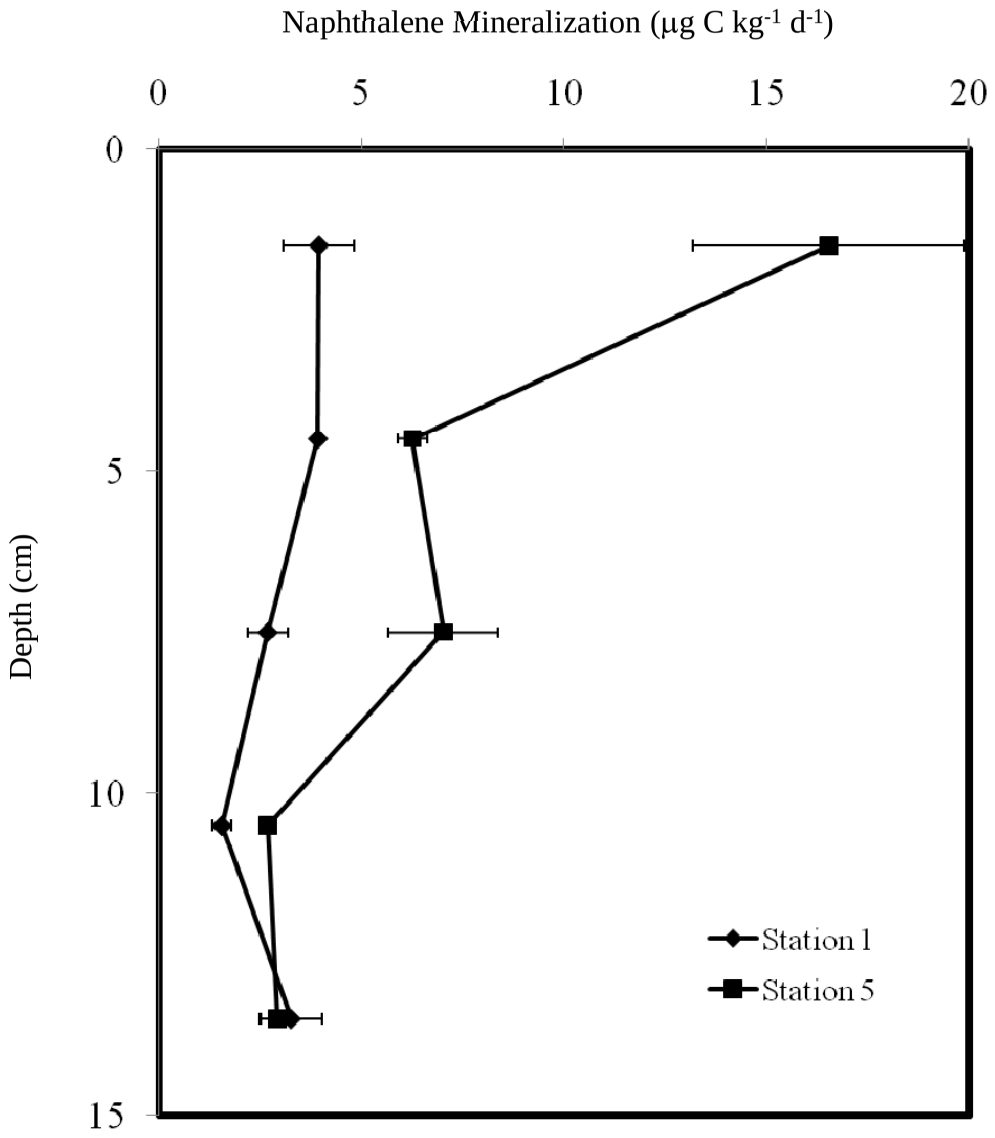

Figure 20. Fluoranthene mineralization rate (µg C kg^{-1} d^{-1}) in surface sediments for three samplings with distance from the Ala Wai Boat Harbor (m).

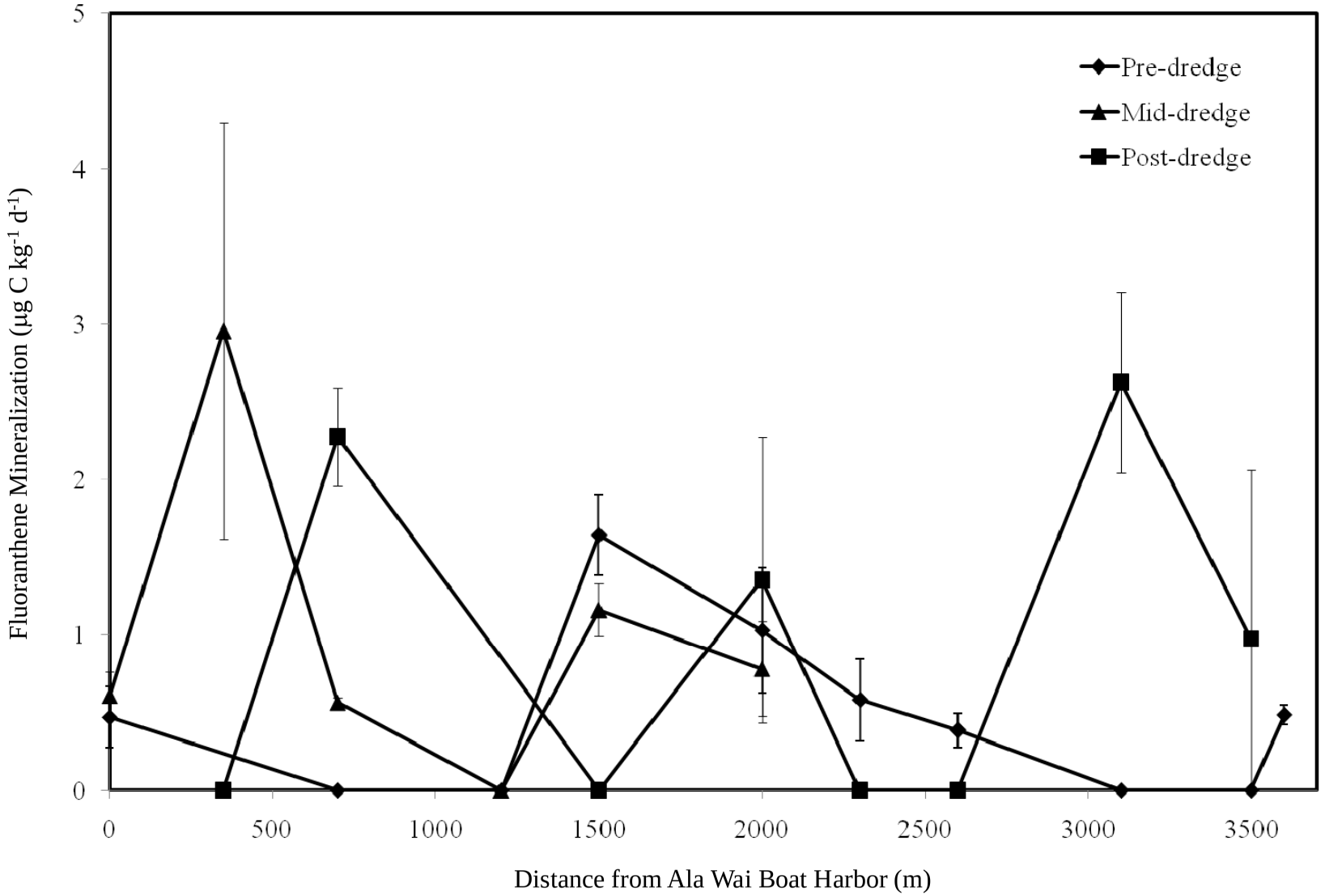

Figure 21. Fluoranthene mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the pre-dredge June 2002 sampling.

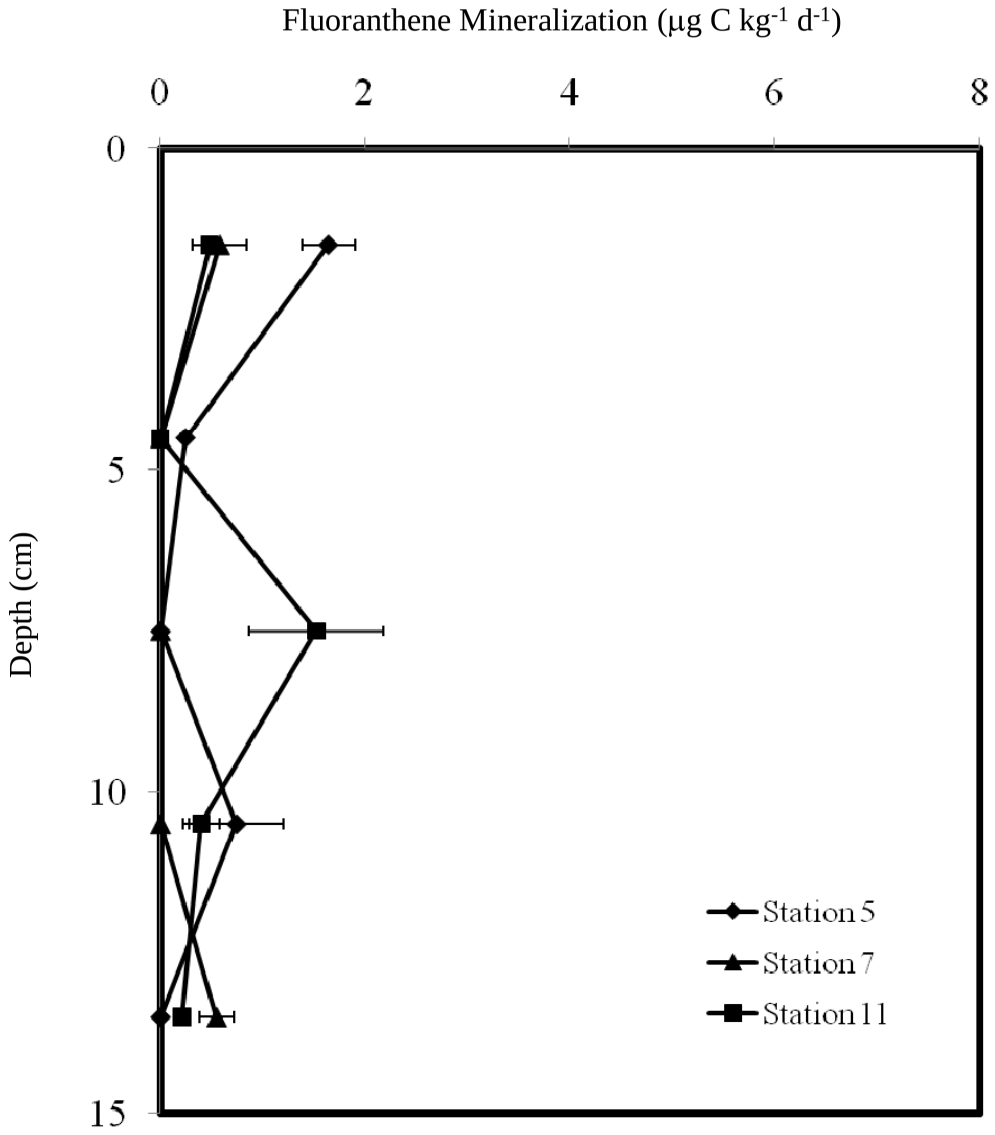

Figure 22. Fluoranthene mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for two cores taken during the mid-dredge February 2003 sampling.

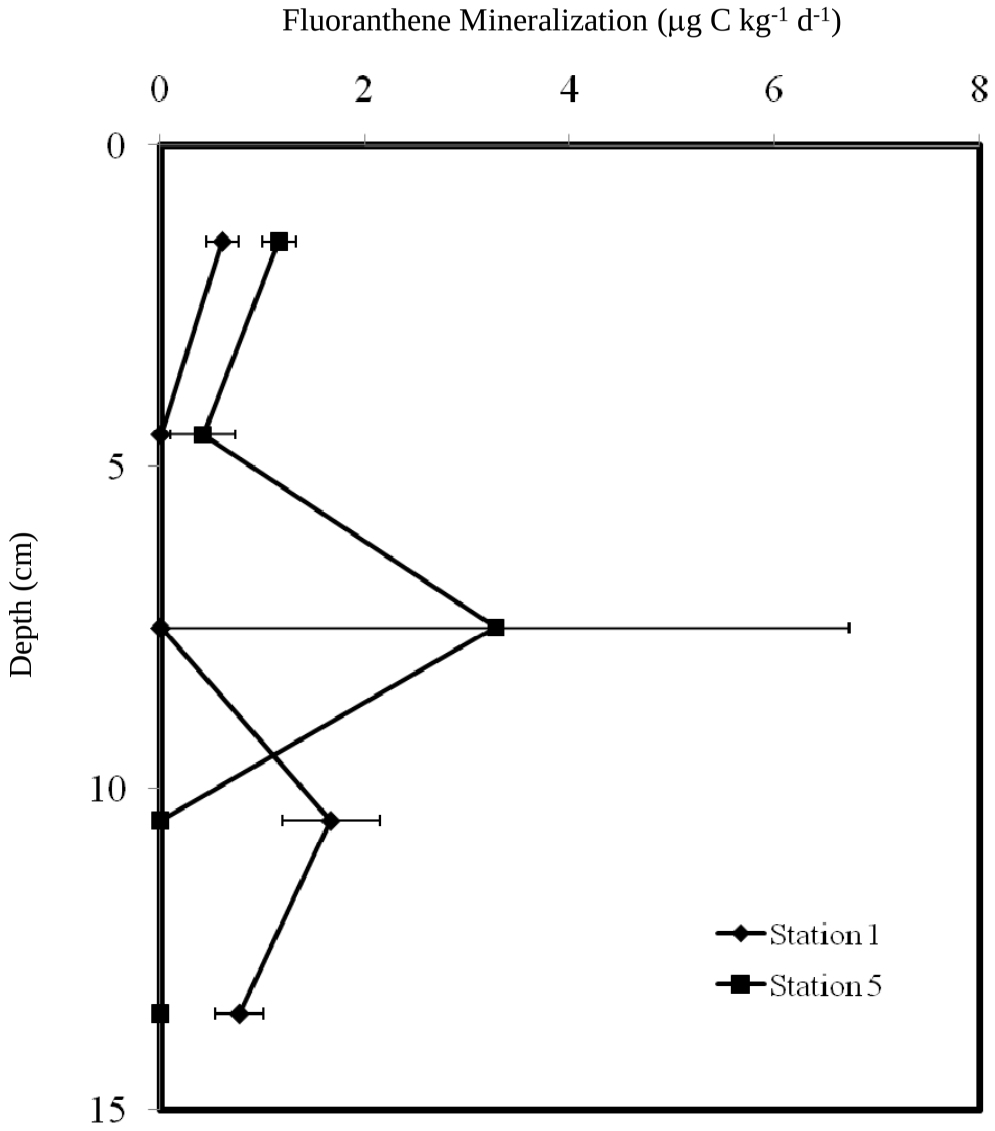

Figure 23. Fluoranthene mineralization (μg C kg^{-1} d^{-1}) with depth (cm below sediment-water interface) for three cores taken during the post-dredge December 2003 sampling.

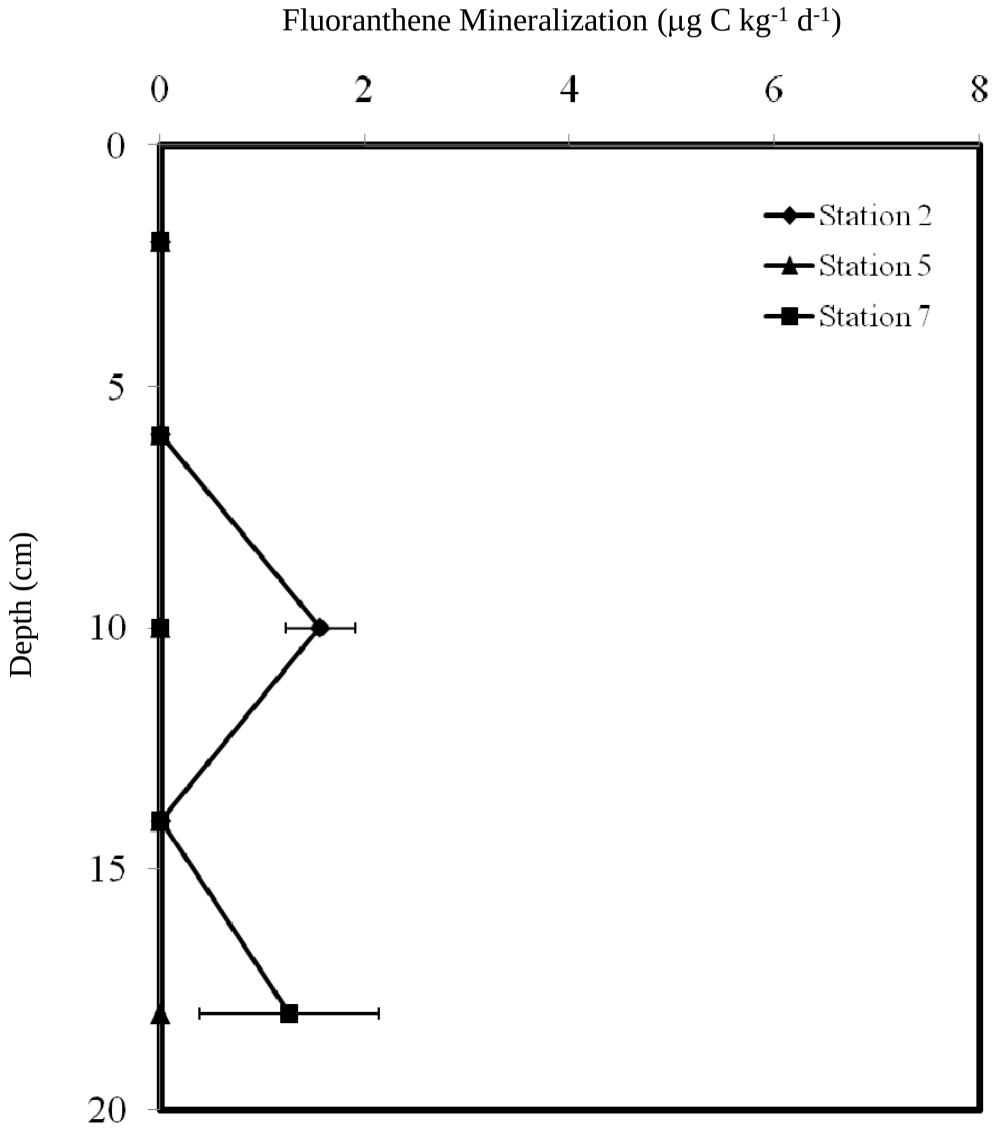

Figure 24. Surface sediment concentration of all eight lignin-derived phenols, S8, (mg per g dry weight^{-1}) and of only the six syringyl and vanillyl phenols, L6 (mg per 100 mg organic carbon) for the pre-dredge June 2002 sampling.

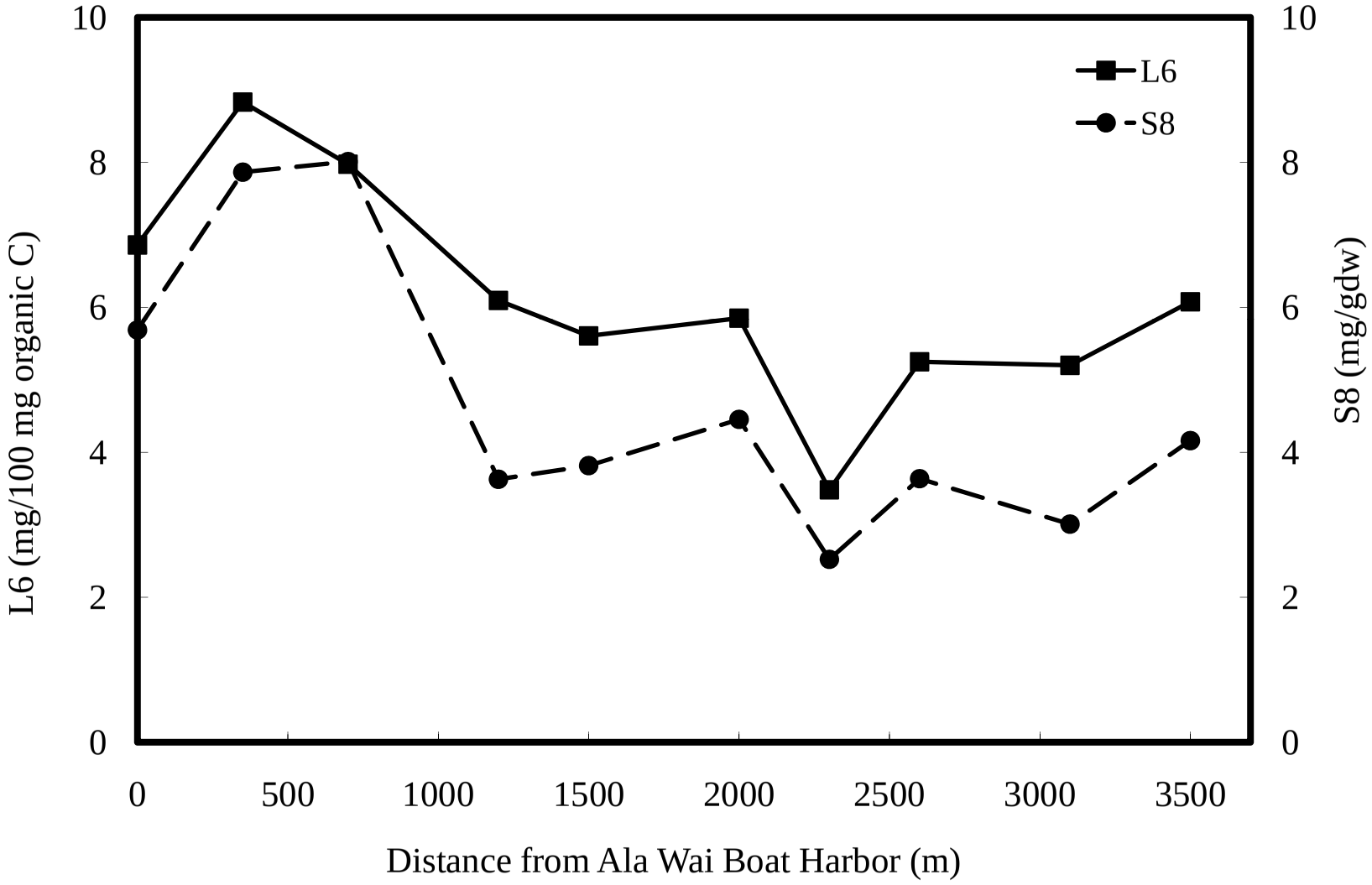

Figure 25. S/V and C/V ratios of lignin-derived phenols from surface sediments of the pre-dredge June 2002 sampling.

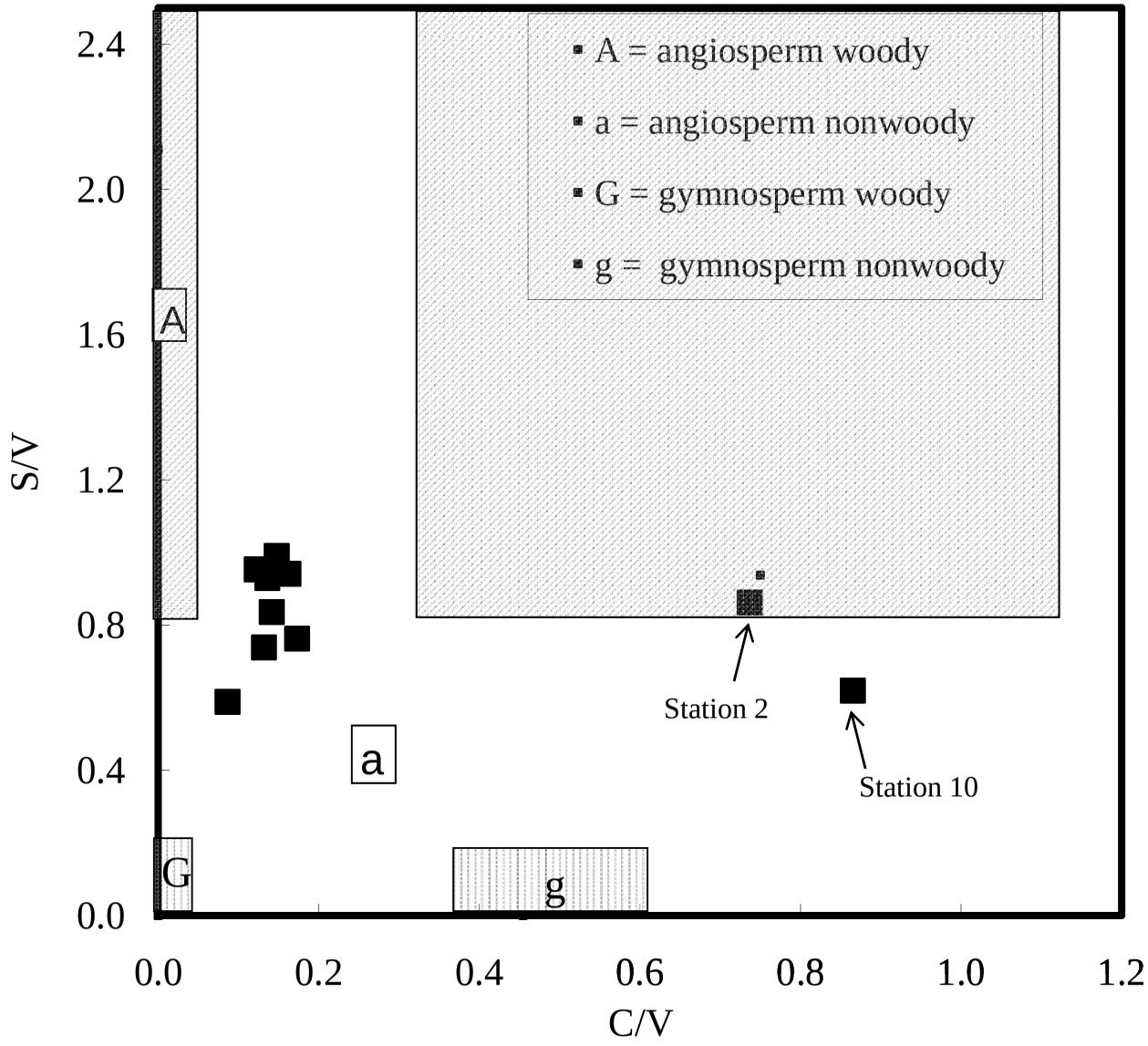

Figure 26. Lignin phenol concentration (S8, mg g^{-1} dry weight), catechol mineralization rate (μg g^{-1} d^{-1}), and ratio of to aldehyde for the vanillin family of lignin phenols ([Ad/Al]v) for the pre-dredge June 2002 sampling.

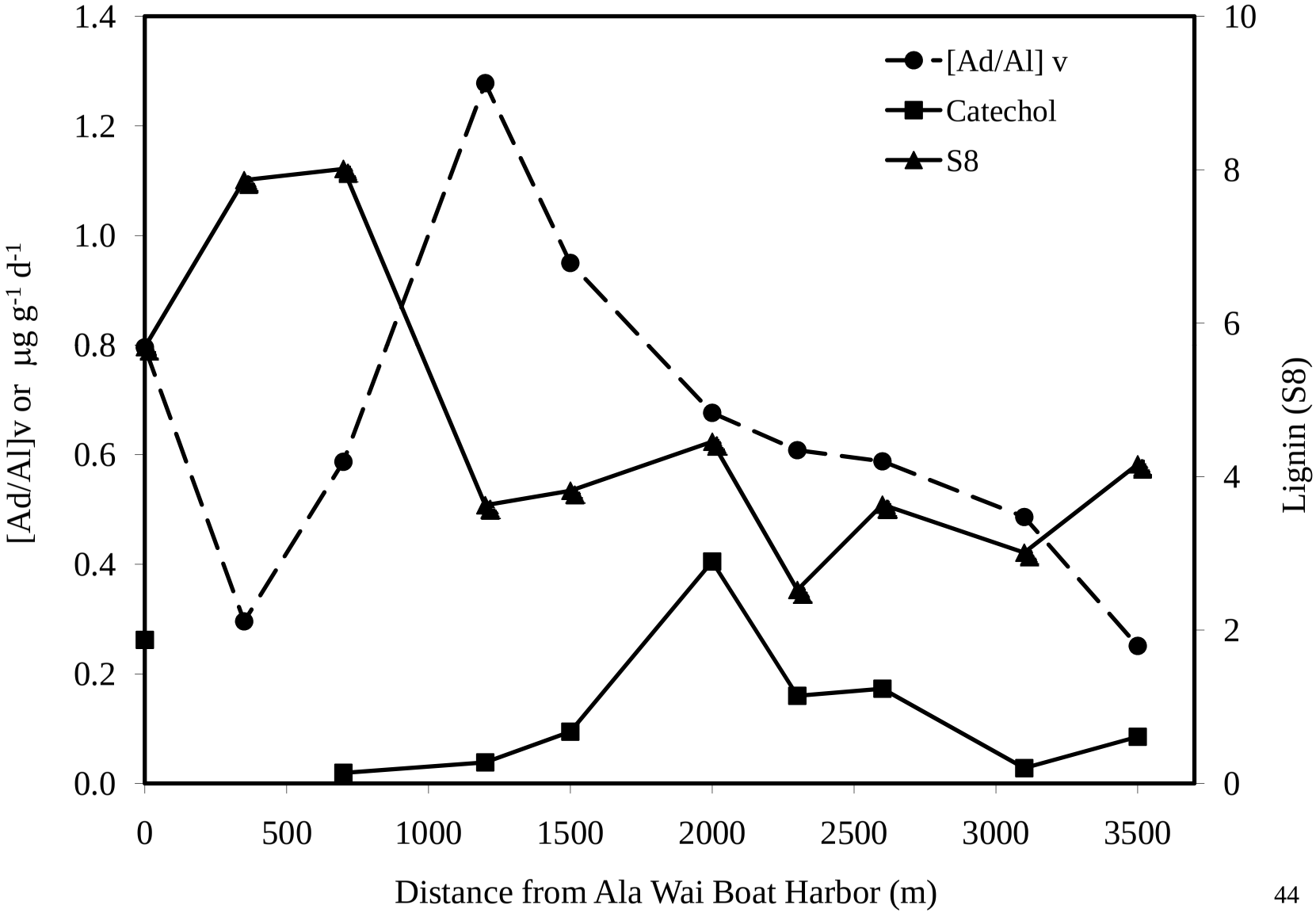

Figure 27. Carbon to nitrogen ratios of organic matter in surface sediment for pre-dredge (June 2002) and post-dredge (December 2003) samplings.

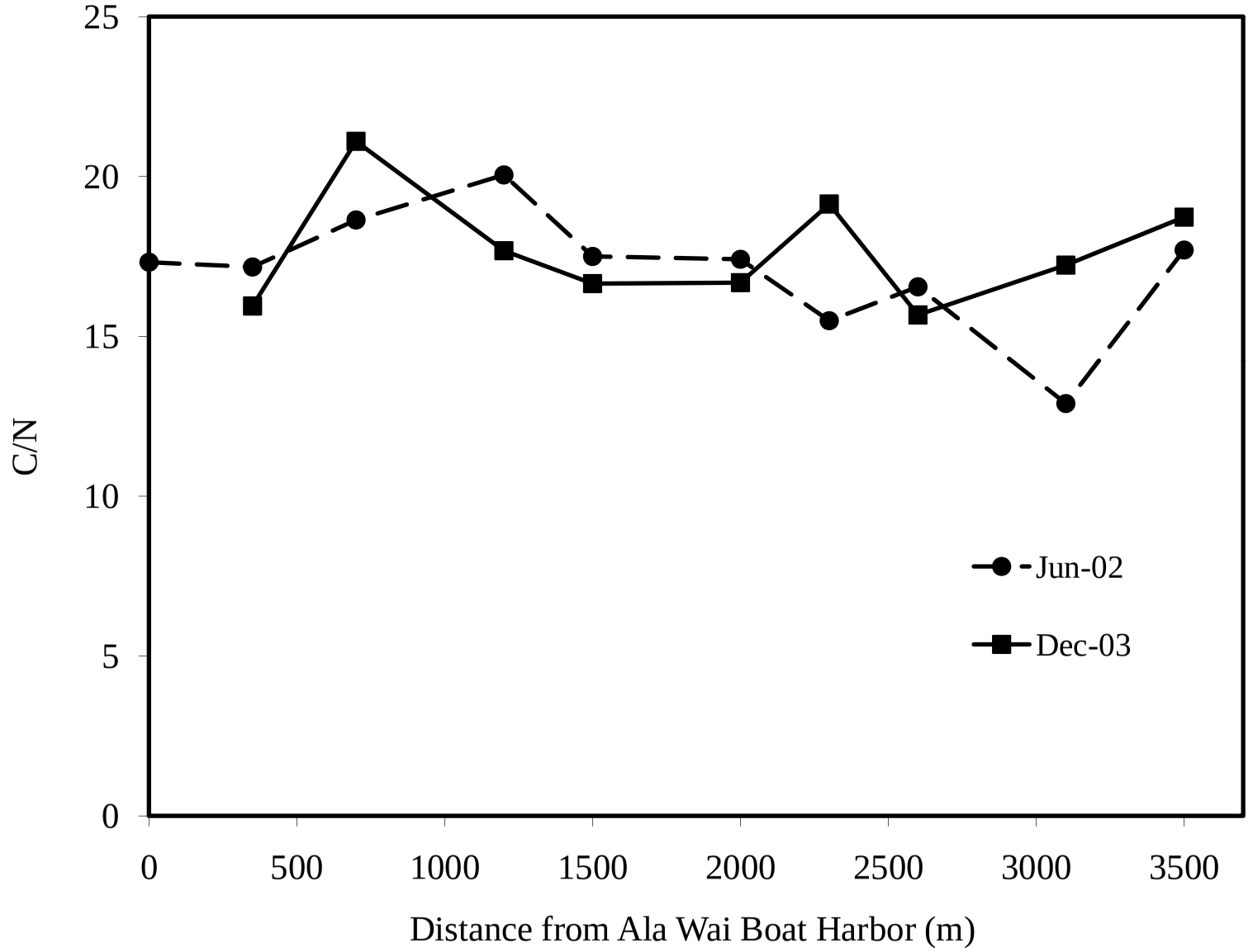

Figure 28. Organic carbon (%) for surface sediment collected during the pre-dredge June 2002 and post dredge December 2003.

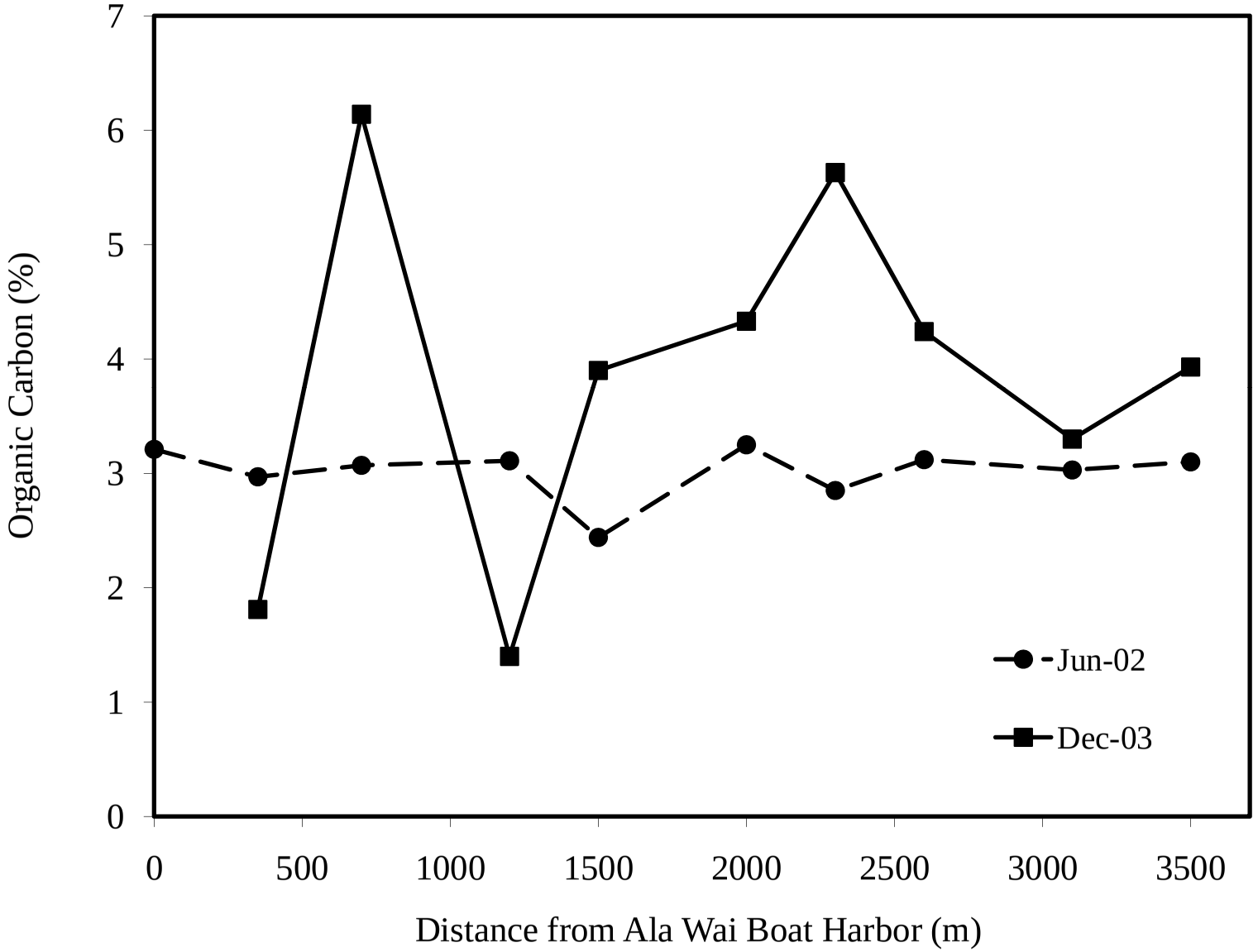

Figure 29. Temperature (°C) of surface, middle and bottom water from post-dredge sampling (December 2003).

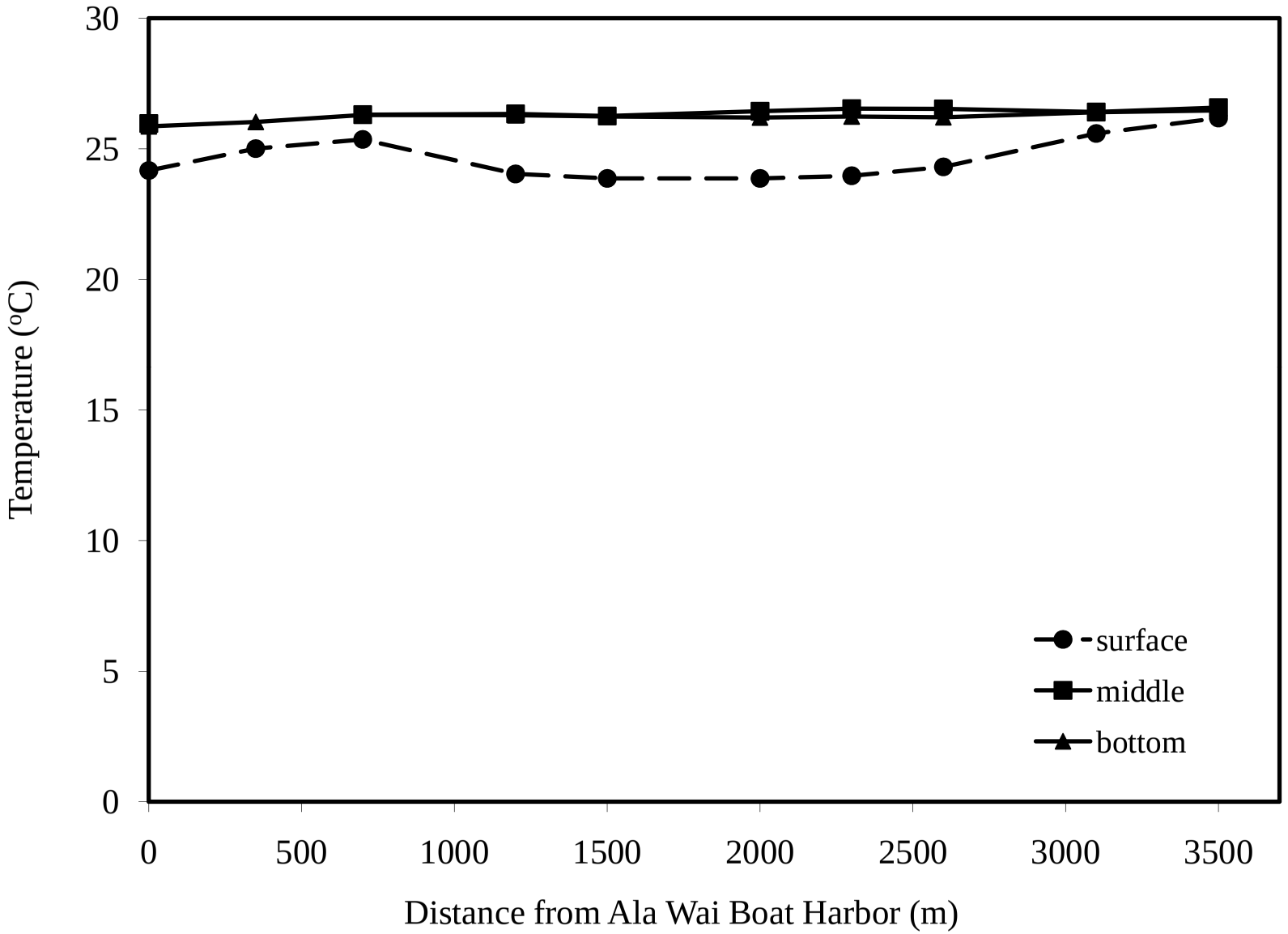

Figure 30. Salinity (PSU) of surface, middle and bottom water from post-dredge sampling (December 2003).

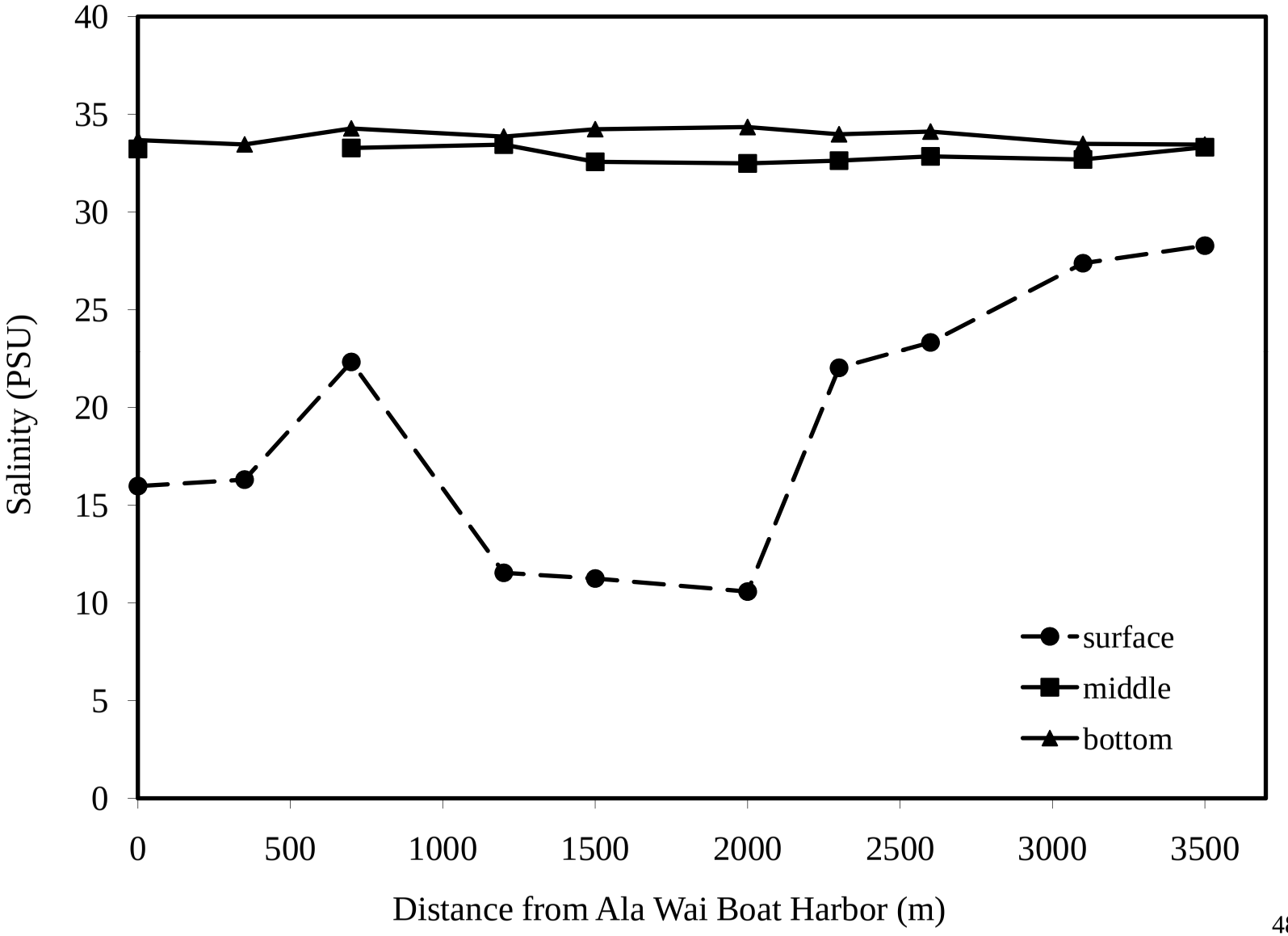

Figure 31. pH of surface, middle and bottom water from post-dredge sampling (December 2003).

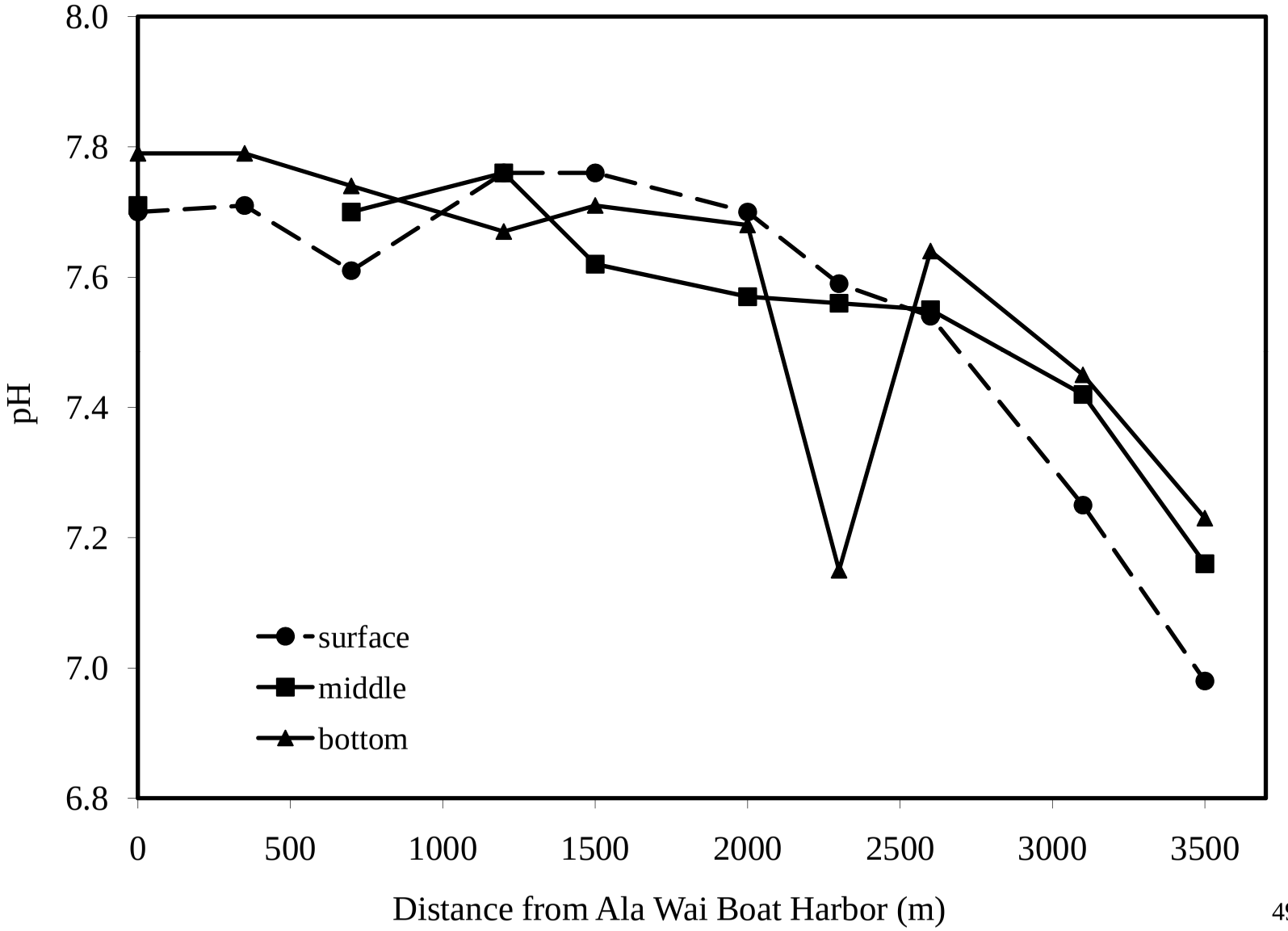

Figure 32. Dissolved oxygen (mg L^{-1}) of surface, middle and bottom water from post-dredge sampling (December 2003).

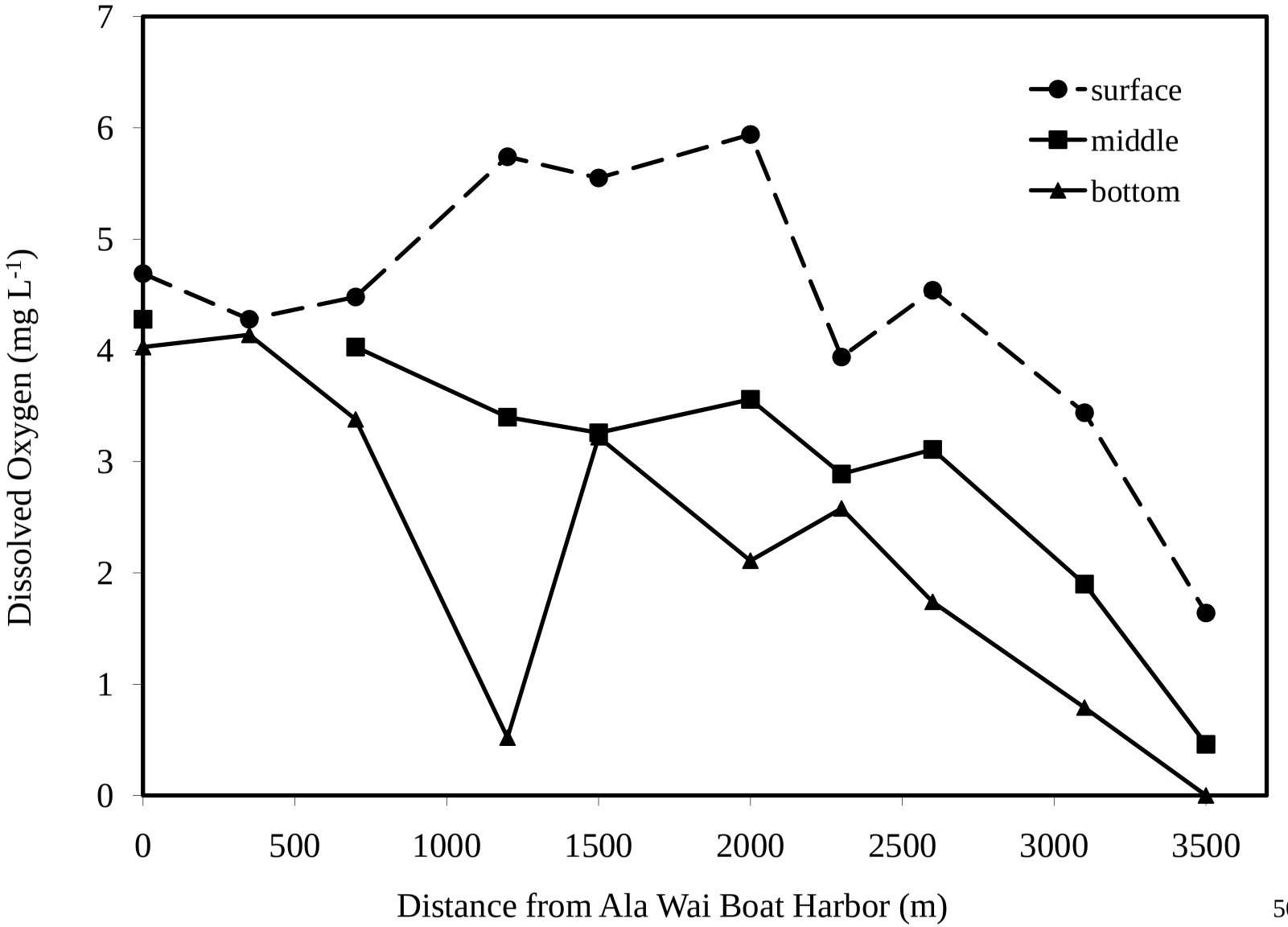

Table 3. Meiofaunal diversity (classified to Order) and abundance for surface sediment of the pre-dredge June 2002 sampling.

Station	Nematoda sp.	Harpacticoid copepods	Polychaeta sp.	Foraminifera sp.	Ostracods	Notes
1	7	3	2	0	1	
2	1	0	0	0	0	Lots of organic matter
3	1	0	2	0	0	Fine org matter
4	28	44	31	4	2	Lots orf org matter;large proportion of polychaetes were larvae
5	0	0	1	0	0	Fine sed; mostly org matter; lost about 1/2 sample
6	0	1	8	0	0	Fine org matter
7	3	7	6	0	1	Fine sed; mostly org matter
8	0	0	0	0	0	No animals;fine sed; mostly org matter
9	0	0	0	0	0	No animals;fine sed; mostly org matter
10	7	0	3	0	0	Lots of organic matter

Table 4. Primary and secondary production rates in water and surface sediment compared with those in the literature for the Ala Wai and other coastal Hawaiian areas.

Location (month)	**Heterotrophic Bacterial (Secondary) Production**		**Water Column Primary Production** ($\mu g\ C\ L^{-1}\ d^{-1}$)	**Reference**
	Water Column ($\mu g\ C\ L^{-1}\ d^{-1}$)	**Surface Sediment** ($\mu g\ C\ kg^{-1}\ d^{-1}$)		
Ala Wai Canal	---	---	ca. 2650	Harris 1975
Ala Wai Canal	2400-2850*	---	675-3000	Laws et al. 1993
Ala Wai Canal (6/02)	---	13-126	---	*This study (pre-dredge)*
Ala Wai Canal (2/03)	---	<1-23	---	*This study (mid-dredge)*
Ala Wai Canal (12/03)	---	33-412	---	*This study (post-dredge)*
Kahana Bay (5/06)	1.7-6.8	---	---	Montgomery et al. 2008
Kahana Bay (8/07)	24-71	42-121	---	Montgomery et al. 2010
Mamala Bay (5/05)	1.3-4.8	---	1900-4600	Walker et al. 2006
Pearl Harbor (12/02)	---	23-38	---	Montgomery and Osburn 2004
Various offshore locations and depths (8/99, 10/00)	0.06-4.3	---	---	Coffin et al. 2004

*includes respiration from phytoplankton

Table 5. Carbon substrate mineralization rates in surface sediment compared with those in the literature for the Ala Wai and other coastal Hawaiian areas (ND=Not detected).

Location	**Mineralization** (μg C kg^{-1} d^{-1})					**Reference**
	Catechol	**TNT**	**Phenanthrene**	**Naphthalene**	**Fluoranthene**	
Ala Wai Canal (6/02)	19-405	---	ND-89	0.06-6	ND-2	*This study (pre-dredge)*
Ala Wai Canal (2/03)	ND-1528	---	ND-73	0.3-17	ND-3	*This study (mid-dredge)*
Ala Wai Canal (12/03)	ND-650	ND-17	ND-49	---	ND-3	*This study (post-dredge)*
Kahana Bay (8/07)	---	8-50	---	---	---	Montgomery et al. 2010
Pearl Harbor (2/99)	---	---	ND-895	ND-14	ND-2011	Boyd et al. 2008
Pearl Harbor (8/99)	---	---	ND-440	ND-603	ND-2911	Boyd et al. 2008
Pearl Harbor (12/02)	ND-105	3-33	ND-13	0.3-2	0.1-8	Montgomery and Osburn 2004